43361

National Library of Canada | Bibliothèque nationale du Canada

CANADIAN THESES ON MICROFICHE

THÈSES CANADIENNES SUR MICROFICHE

NAME OF AUTHOR/*NOM DE L'AUTEUR* Stephen W Burnie

TITLE OF THESIS/*TITRE DE LA THÈSE* A Sulphur and Carbon Isotope Study of Hydrocarbons from the Devonian of Alberta, Canada

UNIVERSITY/*UNIVERSITÉ* ~~The~~ The University of Alberta

DEGREE FOR WHICH THESIS WAS PRESENTED/ *GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE* PhD.

YEAR THIS DEGREE CONFERRED/*ANNÉE D'OBTENTION DE CE GRADE* 1979

NAME OF SUPERVISOR/*NOM DU DIRECTEUR DE THÈSE* Dr. H. Baadsgaard

Permission is hereby granted to the NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

L'autorisation est, par la présente, accordée à la BIBLIOTHÈQUE NATIONALE DU CANADA de microfilmer cette thèse et de prêter ou de vendre des exemplaires du film.

L'auteur se réserve les autres droits de publication; ni la thèse ni de longs extraits de celle-ci ne doivent être imprimés ou autrement reproduits sans l'autorisation écrite de l'auteur.

DATED/*DATÉ* 79 03 14 SIGNED/*SIGNÉ* Stephen W Burnie

PERMANENT ADDRESS/*RÉSIDENCE FIXÉ* 723 104 Ave SW
Calgary, Alberta
T2W 0A4.

NL-91 (3-74)

National Library of Canada

Cataloguing Branch
Canadian Theses Division

Ottawa, Canada
K1A 0N4

Bibliothèque nationale du Canada

Direction du catalogage
Division des thèses canadiennes

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE

NL-339 (3/77)

THE UNIVERSITY OF ALBERTA

A SULPHUR AND CARBON ISOTOPE STUDY OF HYDROCARBONS FROM THE DEVONIAN OF ALBERTA, CANADA

by

STEPHEN W. BURNIE

©

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT Geology

EDMONTON, ALBERTA
SPRING, 1979

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled, "A Sulphur and Carbon Isotope Study of Hydrocarbons from the Devonian of Alberta, Canada", submitted by Stephen W. Burnie in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

R. St J Lambert
....
Chairman

....

....

H. Baadsgaard
....

G. L. Cumming
....

Date October 4, 1978

....
External Examiner

ABSTRACT

Oils and oil fractions were oxidised for carbon isotope analysis using a wet oxidation and Carius tube procedure. The methods gave accurate isotope values to within ± 0.2°/oo. A method was also developed for the sequential oxidation of the methane, ethane and propane components of a natural gas. The carbon del values of these three paraffin homologs were reproducible to within ± 0.2°/oo.

The variation in the saturate, aromatic, maltene, NSO and sulphur abundances for the Leduc and Keg River oils is controlled markedly by a closed number system effect. A Q-mode factor analysis of the oil fraction and oil sulphur data suggests that maturation and sulphurization are the main processes which affect the composition of the Leduc and Keg River oils. The Leduc oils from the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller hydrodynamic systems form one oil family which can be subdivided into three groups. Group B oils have a composition that is controlled mainly by maturation. This contrasts with the Group C oils whose composition is predominantly related to sulphurization. The third group of oils, A, is essentially a subgroup of B and has been displaced up-dip from deeper, hotter, reservoirs by migrating gas.

Carbon isotope values of the Leduc oils, their saturate and aromatic fractions, and the methane, ethane and propane components of the Leduc natural gases vary as a function of maturation. The magnitude and range in the oil and methane carbon del values indicate that the Leduc hydrocarbons have been derived from marine organic matter of Devonian age. A distinction cannot be made between the Leduc and Keg River oils using the carbon isotope values of the oils or oil fractions. Therefore, either the Leduc and Keg River oils have very similar sources, or carbon isotopes are not suited to some oil correlation problems. The order of C^{12} - enrichment for the Leduc and Keg River natural gas components is: C^{13} (methane) < C^{13} (ethane) < C^{13} (propane). These three gas components were all more C^{12} - enriched than the associated oils. Plots of C^{13} (ethane) and C^{13} (propane) vs. $C_1/C_1 + C_2$ ratios discriminate between Leduc pools in the Homeglen-Rimbey-Redwater system and Leduc pools in the other two systems. The discriminatory ability may result from migration isotope and gas composition fractionation effects. The observed trends in the Leduc hydrocarbons of C^{13} - enrichment in methane and C^{12} - enrichment in the associated oil and saturate and aromatic oil fractions, as the degree of maturation increases, are considered to be interrelated effects which result from the maturation of petroleum in a closed or quasi-closed system.

Variations in the sulphur isotope composition of the Leduc oils are controlled by the maturation and sulphurization processes. Both the magnitude and direction of sulphur isotope enrichment for co-produced

Leduc sulphur samples is compatible with an equilibrium isotope exchange reaction with hydrogen sulphide. The significant linear correlation between the δS^{34} values of hydrogen sulphide and reservoir temperature, for Leduc pools, can be explained using a closed system model. As a consequence of this model, it is believed that hydrogen sulphide in the Leduc reservoir system is produced from the reduction of sulphate lining vugs and pores. The sulphate reduction reactions are probably abiogenic and are analogous to those described by Toland (1960). Although it cannot be conclusively demonstrated that the Toland reaction is responsible for the generation of significant quantities of hydrogen sulphide in the reservoir system, this reaction has the potential to generate an abundance of sulphur compounds.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my principal supervisor Dr. H. Baadsgaard for his counsel and instruction during the course of this work. Thanks are also due to Dr. R. St J. Lambert, Dr. G. D. Williams, Dr. John Gray, Dr. M. Coleman and Dr. D. C. Herrick.

I am extremely grateful to the following people with whom I have had several informative discussions: Dr. H. R. Krouse, Dr. A. Jobson, Dr. F. D. Cook, C. W. Milner, Dr. E. Harwidge, Dr. E. Nordbrock, Dr. J. Ryan, Dr. P. Kebarle, Dr. J. B. Hyne, Dr. A. D. Bailie, Dr. N. Bailey, J. Hogarth and A. Stelmach. I am very appreciative of the time taken by Dr. E. Klovan from his very busy schedule to critically review a portion of my thesis. I wish to express my thanks to the Alberta Research council, in particular to Dr. B. Hitchon, Dr. George and Dr. A. Blades for guidance during the formative stages of my thesis.

I would like to thank the following oil companies, especially Imperial Oil Enterprises and Gulf Oil of Canada, for providing oil and gas samples for this study: Imperial Oil Enterprises Limited, Gulf Oil Canada Limited, Shell Canada Resources Limited, Aquitaine Company of Canada Limited, Amoco Canada Petroleum Company Limited, Hudson's Bay Oil and Gas Company Limited, Texaco Canada Limited, Union Oil Company of Canada Limited, Canadian Superior Oil Limited, Sun Oil Company

Limited, and Hunt Oil Company. I am grateful to Core Laboratories at Edmonton, in particular to Mr. George Vilsak, without whose liberal provision of sample bombs my sample programme could never have been completed. I am also grateful to the Energy Resources Conservation Board, especially D. R. Shaw, for providing gas analyses for some Leduc pools.

A debt of gratitude is owing to Dr. H. P. Schwarcz of McMaster University and Dr. Peter Fritz of the University of Waterloo for permitting my use of their mass spectrometers during the early stages of my thesis. I would like to thank the Department of Microbiology at the University of Alberta, especially Dr. D. W. S. Westlake, for use of their chromatography facilities. Thanks are also due to the Thode Laboratory at McMaster University for providing sulphur isotope standards.

I would like to thank my present employer, Amoco Petroleum Company, for providing isotope analyses of gas standards, and for use of their computing, word processing, drafting and reproduction facilities.

I am very grateful for financial support from the National Research Council of Canada, the Petroleum Aid to Education Fund and Imperial Oil Enterprises Limited.

To my wife Kelly, daughter Katherine and son Stephen I would like to extend my fondest thanks for their patience and understanding throughout the course of this work.

TABLE OF CONTENTS

PAGE

INTRODUCTION 1

a) An Overview . . . .
b) Geologic Setting . . . .
c) Required analytical procedures . . . .
d) Coda . . . .

PART I

ANALYTICAL PROCEDURES, EXPERIMENTAL ERROR AND MASS SPECTROMETER CALIBRATIONS

CHAPTER

I. EXPERIMENTAL PROCEDURES, ANALYSIS OF ERROR AND RELEVANT DISCUSSIONS 11

Section 1: Gas, Oil and Water Sampling Procedures 11

Section 2: Extraction of Sulphur Compounds from Natural Gases and Formation Waters 16

a) Recovery of Sulphides from Natural Gases and Formation Waters 16

b) Recovery of Sulphur Compounds from Formation Water 19

Section 3: Extraction of Oil Sulphur and Its Preparation for Isotope Analysis 24

a) Total Sulphur Extraction from Oils 24

b) Conversion of Sulphate to Silver Sulphide . . . 26

c) Conversion of Silver Sulphide to SO_2 31

Section 4: Oxidation of Oils for Carbon Isotope Analysis . . . 35

a) Introduction 35

PAGE

Section 4: (Cont'd)

b) Wet Oxidation Procedure 36

c) Carius Tube - Cupric Oxide Oxidation Method . . 46

Section 5: Separation and Combustion of Natural Gas Components 56

a) Introduction 56

b) Gas Chromatograph Design 57

c) Gas Component Combustion System Design 65

d) Chromatograph Design Restrictions 71

e) Gas Sample Injection 72

f) Gas Component Combustion 73

g) Isolation and Purification of Combustion Products 74

h) Carbon Isotope Reproducibility and Accuracy of the Copper(II) Oxide Combustion Furnace Method 75

Section 6: Procedures for the Liquid Chromatography of Oils and the Gas - Liquid Chromatography of the Saturate Fraction 80

a) Liquid Chromatography of Oils 80

b) Gas - Liquid Chromatography of the Saturate Fraction 82

c) Error Calculations for the Liquid and Gas - Liquid Chromatograph Analyses 85

CHAPTER

II MASS SPECTROMETER CALIBRATION AND CORRECTION EQUATIONS 89

Section 1: Introduction 89

PAGE

CHAPTER

II (Cont'd)

Section 2: Sulphur Isotope Correction and Calibration Equations 90

Section 3: Carbon Isotope Correction Equation 98

PART II

GEOCHEMISTRY OF HYDROCARBONS
IN THE DEVONIAN OF CENTRAL ALBERTA

CHAPTER

I. Introduction - THE LEDUC REEF SYSTEM, SAMPLE PROGRAMME AND OIL SULPHURIZATION REACTIONS 106

Section 1: Geology and Geochemistry of the Leduc Reef System 106

Section 2: Sample Locations 114

Section 3: An Introduction to the Petroleum Sulphur System . . . 115

CHAPTER

II GEOCHEMISTRY OF D-3 OILS 126

Section 1: Oil Composition 126

a) Closed Number System 130

b) Q-Mode Factor Analysis of the Oil Fraction Data 137

c) Interpretation of the Q-Mode Factors 144

d) Biodegradation of D-3 and Keg River Oils 155

e) Oil Families 160

Section 2: Sulphur Isotopes of D-3 and Keg River Oils 162

Section 3: Carbon Isotopes of D-3 and Keg River Oils 184

PAGE

CHAPTER

III STABLE ISOTOPE COMPOSITION OF D-3 NATURAL GASES 201

Section 1: Introduction 201

Section 2: Sulphur Isotope Composition of D-3 and Keg River Natural Gases and Associated Sulphur Species 205

a) Sulphur Isotope Distribution for Sour D-3 and Keg River Natural Gases 205

b) Temperature Dependence of the Sulphur Isotope Composition of Sour Natural Gases - the Closed System Model 213

c) The Hydrocarbon Sulphur System - A Model 244

Section 3: Carbon Isotope Composition of D-3 Natural Gases . . . 256

***

CONCLUSIONS 284

REFERENCES 290

APPENDICES 303-339

LIST OF TABLES

Table	Description	Page
	PART I	
I-I	Comparison of Sulphur Isotope Values for Chromatographed Hydrogen Sulphides and Total Sulphide Precipitates from Natural Gases	18
I-II	Yields and Sulphur Isotope Analyses for Replicate Sulphate and Sulphide Reductions	30
I-III	Duplicate Carbon Percents and δC^{13} Values for Oils Oxidised Using the Wet Oxidation Method	44
I-IV	Replicate Carbon Yields for $Cd(CH_3COO)_2$	45
I-V	Mean δC^{13}_{PDB} Values for Imperial Oil Laboratory Standards	45
I-VI	Carbon Isotope Analyses of NBS Oil No. 22	54
I-VII	Chromatograph Specifications	62
I-VIII	Selected Retention Times	64
I-IX	Oxidation Efficiency of the CuO Furnace	70
I-X	Carbon Isotope Analyses of Duplicate Burns of Methane, Ethane and Propane Gases	77
I-XI	Reproducibility of Oil Fraction Percents Determined by Liquid Chromatography	86
I-XII	Data for the Sulphur Isotope Correction and Calibration Equation	95
I-XIII	Average R^{13}, R^{17} and R^{18} Values for Standard Gases and Oxidation Reagents	102

Table	Description	Page
	PART II	
II-I	Reservoir Statistics for D-3 Pools	112
II-II	Selected Leduc Reef Solution Gas Analyses	118
II-III	Oil Component Analyses	127
II-IV	Normalized Average Oil Composition for D-3 Pools	133
II-V	Closed System Factors Calculated from the Composition of the Big Lake and Westerose Oils	134
II-VI	Closed System Factors Calculated from the Composition of the Big Lake and Buffalo Lake Oils	135
II-VII	Closed System Factors Calculated from the Composition of the Big Lake and Wizard Lake Oils	136
II-VIII	Eigen Values	141
II-IX	Varimax Factor Matrix for Three Factors	142
II-X	Varimax Factor Scores Matrix	147
II-XI	Sulphur Isotope Values for Albertan Devonian Oils, Sour Non-associated Gases and Solution Gases, and Related Aqueous Sulphides and Brine Sulphates	163
II-XII	Sulphur Isotope Values for Albertan Devonian Oils, Sour Non-associated Gases and Solution Gases, and Related Aqueous Sulphides and Brine Sulphates	209
II-XIII	Mean Square Deviations for δS^{34} (RGS)	229
II-XIV	Sulphate Concentration of D-3 Formation Waters	235
II-XV	Natural Gas Analyses from Metamorphosed Reservoirs	254
II-XVI	Average δC^{13} Values for Devonian Oil and Gas Pools	258
A-I	List of Stopcock Settings for the Chromatograph and Combustion Apparatus	317
A-II	Data from Dhannoun and Fyfe (1972)	338

LIST OF FIGURES

Figure Page

PART I

I-1 Gas Storage Container 12

I-2 Gas Sample Transfer Apparatus 13

I-3 Stopcock Flow Positions 14

I-4 Histogram of Mean S% in Oils 25

I-5 Yield Histogram for the Sulphate Reduction Line 29

I-6 Histogram Ag_2S - Copper Oxide Burn Yields 33

I-7 Side View of a Glass Button Sample Container 37

I-8 Side View of a K-Form Reaction Vessel 38

I-9 Vacuum Extraction and Preparation Apparatus 39

I-10 Side View of a K-Form Reaction Vessel Modified for Extraction 41

I-11 Carius Tube Reaction Vessel 48

I-12 Evacuated Tube Containing CuO and the Oil Sample 49

I-13 Plot of Reaction Time vs. δC^{13}_{PDB} for NBS Oil No. 22 51

I-14 Natural Gas Component Separation and Combustion Apparatus 58

I-15 Natural Gas Chromatogram 63

I-16 Oxidation Tube Description 68

I-17 Natural Gas Chromatogram - Precombustion 67

I-18 Chromatogram of Combusted Redwater Sales Gas 68

I-19 Combustion Products Separation Line 76

I-20 Saturate Profile OV-101 Column 84

Figure Page

I-21 Saturate Profiles 88

I-22 Sulphur Isotope Calibration and Correction Equation 96

PART II

II-1 Leduc Reef Distribution 108

II-2 Subdivisions of the Leduc Formation 109

II-3 Plot of the Normalized Varimax Factor Components for Three Factors 141

II-4 Plot of Varimax Factor I Loadings versus Formation Temperature 146

II-5 Plot of the Scaled Normalized Oil Saturate Content vs. Formation Temperature 149

II-6 Plot of the n-C_{16}/n-C_{31} Ratio vs. Factor I Saturate Loading for D-3 Oils 151

II-7 Plot of the Phytane/n-C_{18} Ratio vs. Factor II Content of D-3 Oils 154

II-8 N-Alkane Distribution in "Topped" Leduc and Keg River Oils 157

II-9 Plot of the Phytane/n-C_{18} Ratio vs. Factor I Content of D-3 Oils 158

II-10 Sulphur Isotope Values for Devonian Oils in Alberta 167

II-11 Plot of δS^{34} vs. Factor I Content for D-3 and Keg River Oils 169

II-12 Plot of δS^{34} vs. Average Maturation Temperature for D-3 Oils. R is the Linear Correlation Coefficient 173

II-13 Generalized Source Rock Sulphur System 175

II-14 Generalized Reservoir Sulphur System 179

II-15 Plot of Pool Av. δS^{34} Value vs. Present Day Reservoir Temperature 183

Figure Page

II-16 Carbon Isotope Values for D-3 and Keg River Oils in Alberta 185

II-17 Plot of δC^{13} (Saturates) - δC^{13} (Aromatics) vs. Varimax Factor I Components for D-3 and Keg River Oils 188

II-18 Plot of δC^{13} (Saturate Fraction) vs. the Varimax Factor I Component for Keg River and D-3 Oils 191

II-19 Plot of δC^{13} (Aromatic Fraction) vs. the Varimax Factor I Component for Keg River and D-3 Oils 192

II-20 Plot of δC^{13} (Whole Oil) vs. Factor I for D-3 and Keg River Oils 193

II-21 Plot of Initial GOR vs. % Maltenes 195

II-22 Plot of δC^{13} (Whole Oil) vs. Initial GOR for D-3 Oils 196

II-23 Plot of the Paraffin n-C_{16}/n-C_{30} Ratio vs. Initial GOR for D-3 Oils 197

II-24 Plot of δC^{13} (Saturates) vs. δC^{13} (Aromatics) for Devonial Oils 199

II-25 δS^{34} Distribution for Keg River and D-3 Sour Non-Associated and Solution Gases, and Related Sulphur Species 206

II-26 Plot of δS^{34} of the Total Gaseous Sulphide vs. Present Day Reservoir Temperature for D-3 Pools 214

II-27 Plot of Δ vs. f for $\alpha = 1.022$ 223

II-28 Plot of Mole Percent Hydrogen Sulphide versus Present Day Reservoir Temperature for D-3 Pools 224

II-29 Plot of Mole Percent Hydrogen Sulphide versus δS^{34} (Hydrogen Sulphide) for D-3 Pools 225

II-30 Comparison of D-3 RGS Sulphur Isotope and Reservoir Temperature Data to the Closed System Relationship 228

II-31 Plot of Δ vs. 1/T for Equilibrium and Kinetic Isotope Models 231

Figure Page

II-32 Plot of Present Day Reservoir Temperature vs. Estimated Maximum Reservoir Temperature from Coal Rank Data, for D-3 Pools 233

II-33 Plot of δS^{34} Gas Sulphur vs. δS^{34} Oil Sulphur for D-3 Reefs 238

II-34A Sulphur System Reaction Scheme I 249

II-34B Sulphur System Reaction Scheme II 249

II-35 Reaction Scheme III - The Toland Model for the Generation of Sulphur Compounds in the Hydrocarbon Reservoir System 252

II-36 Carbon Isotope Values for D-3 and Keg River Natural Gas Components 257

II-37 Plot of the Carbon Isotope Value (δC^{13}_{PDB}) of D-3 Methane vs. $C_1/C_1 + C_2$ Ratio 261

II-38 Plot of the Carbon Isotope Composition of Ethane vs. $C_1/C_1 + C_2$ 267

II-39 Plot of the Carbon Isotope Composition of Propane vs. $C_1/C_1 + C_2$ 268

II-40 Plot of δC^{13} (Methane) - δC^{13} (Ethane) vs. $C_1/C_1 + C_2$ Ratio 272

II-41 Plot of δC^{13} (Methane) - δC^{13} (Propane) vs. $C_1/C_1 + C_2$ 273

II-42 Plot of δC^{13} (Ethane) - δC^{13} (Propane) vs. $C_1/C_1 + C_2$ 274

II-43 Plot of δC^{13} (Whole Oil) vs. δC^{13} (Methane) for D-3 Oils and Gases 276

II-44 Plot of δC^{13} (Aromatics) vs. δC^{13} (Methane) for D-3 Oils and Gases 277

II-45 Plot of δC^{13} (Aromatics) vs. δC^{13} (Ethane) for D-3 Oils and Solution Gases 279

II-46 Plot of $\text{Log}/\Delta/$ vs. f for the Pyrolysis of Neopentane 281

Figure

Page

II-47 Plot of Δ Methane vs. Δ Pentane 282

A-1 Sample Transfer Apparatus 313

A-2 Natural Gas Component Separation and Combustion Apparatus 316

A-3 Combustion Products Separation Line 321

LIST OF ENCLOSURES

Enclosure	Description	Page
1a	Location of Alberta Oil Fields	
1b	Map of Alberta Oil and Gas Fields	

INTRODUCTION

a) An Overview

As early as 1958, Thode et al. (1958) demonstrated that sulphur isotopes could be used to distinguish between oils from different source rocks. However, Vredenburg and Cheney (1971) and Orr (1974) clearly established that oil sulphur isotope composition was not only a function of source, but also a function of maturation. Furthermore, the available literature on the subject provides no single answer regarding time of oil sulphurization. If oil is sulphurized in the reservoir, its sulphur isotope composition would be characteristic of the reservoir sulphur source and not necessarily the oil source. Therefore, the situation could arise where oils from different source rocks have the same sulphur isotope composition. The use of sulphur isotopes to correlate between crude oils is therefore problematic and requires clarification.

The variation of the sulphur isotope composition of hydrogen sulphide in natural gases as a function of reservoir temperature and the related property of reservoir maturity is now well documented (Vredenburg and Cheney, 1971; Orr, 1974; Orr, 1975; Burnie, 1975; Hitchon et al., 1975). However, at the inception of this thesis, the documentation was far less complete. Prior to a publication by Orr (1974) hydrogen sulphide in the reservoir system was believed to be produced by sulphate reducing bacteria and/or generated by the desulphurization of petroleum. However, biogenic hydrogen sulphide cannot be produced in abundance at temperatures in excess of 60°C (Jobson, 1976). Furthermore, oils are more reactive to sulphur compounds at higher reservoir temperatures, which appears to contradict the desulphurization concept. Orr (1974) proposed a two part model for the generation of hydrogen sulphide. At low reservoir temperatures, hydrogen sulphide could be produced by sulphate reducing bacteria. At higher reservoir temperatures (80 to 120°C) hydrogen sulphide was postulated to be generated by a Toland-type abiotic reduction of sulphate by hydrogen sulphide (see Toland, 1960) for which there was no sulphur isotope fractionation. Therefore, the observed variation in the sulphur isotope composition of hydrogen sulphide (Orr, 1974) had to be produced during the associated oil sulphurization reactions. However, experimental data from Husain (1967) indicated that the reduction of sulphate by hydrogen sulphide has an accompanying sulphur isotope fractionation effect of 1.022. Furthermore, preliminary results from this thesis showed that there was no correlation between δS^{34} (oil) and δS^{34} (H_2S). A model for the generation of hydrogen sulphide in the reservoir system has to be constructed to resolve the aforementioned contradictions.

Carbon isotope data from oils, oil fractions and the methane, ethane and propane components of associated and non-associated natural gases can provide information regarding oil to oil correlations, oil and gas source rock environment (marine or non-marine) and the degree of maturity of the hydrocarbon deposit and source rocks.

Silverman (1964) used carbon isotopes to distinguish between marine and non-marine oils of Tertiary age. However, Galimov (1973) found the carbon isotope composition of marine and non-marine Carboniferous oils to be indistinguishable. Stahl (1977) noted that the carbon isotope composition of methane associated with mature oils, whose source rock was marine organic matter, was around -45^{o}/oo. With progressive maturation this methane became more C^{13} - enriched, attaining an average carbon del value near -30^{o}/oo in overmature (metamorphosed) reservoirs. The average carbon isotope value for methane derived from marine source rocks is about 13 to 14 per mil more enriched in C^{12} than the average carbon isotope composition of methane gas derived from non-marine or paralic organic matter. Degens (1969) documented a cyclic-temporal variation in the carbon isotope composition of crude oils ranging in age from the Tertiary to the Cambrian. Koons *et al.* (1974) discriminated between oils from different source rocks using a plot of δC^{13} (saturates) versus δC^{13} (aromatics). Stahl (1977) distinguished between oils from different source rocks using petroleum type-curves. However, Koons et al. (1974) and Feux (1977) found variations in the carbon isotope composition of whole oils and oil fractions that could be related to maturation. Therefore, saturate versus aromatic isotope plots are preferred since they are suited to the definition and correlation of oil families.

The variation in the abundance of the saturate, aromatic, asphaltene and NSO oil fractions can be used to characterise processes such as maturation, deasphalting and biodegradation (Evans et al., 1971; Milner et al., 1977). By analysing oil sulphur contents, the sulphurization process can be documented to some degree (Ho et al., 1974). Unfortunately, the oil fraction and sulphur percentage data are influenced markedly by the closed number system effect (Chayes, 1960; Chayes, 1962; Chayes, 1970). It is therefore preferable to use these analyses as part of a Q-mode factor analysis data matrix and use the extracted factors to study the various processes that affect oil composition. However, the extracted factors are still affected, to some degree, by closure.

The chromatography of the saturate oil fraction can be used to distinguish between biodegraded and non-biodegraded oils (Winters and Williams, 1969; Jobson et al., 1972; Bailey et al., 1973). Generally, non-biodegraded oils have a saturate profile with an abundance of C_{15}+ peaks on a broad semi-circular napthenic base.

Strongly biodegraded oils are characterized by a saturate profile consisting of a few heavy (C_{25}+) paraffin peaks and pronounced pristane and phytane peaks which are perched on a compressed and peaked napthenic base.

Oils and gases can experience changes in their composition and undergo carbon and sulphur isotope fractionation as a result of the physical and chemical processes that affect them during migration (Silverman, 1965; Colombo _et al_., 1966; Colombo _et al_., 1969; Stahl, 1977; Milner, 1977). Current opinion considers migration isotope fractionation to have an effect of no more than 1 to 2 per mil on the carbon and sulphur isotope composition of natural gas (Stahl, 1977; Feux, 1977; Krouse, personal communication). For oils which migrate as slugs (see Levorsen, 1967) any migration carbon isotope fractionation should be minimal. Silverman (1965) postulated a migration fractionation effect of around 0.4^{o}/oo for oils migrating up dip in the Quiriquire field in Venezuela.

Therefore, the initial objectives of this research were to study the maturation, migration and alteration[+] history of hydrocarbons, define their source (and its age), and correlate between pools and

---

[+] Alteration in this thesis denotes a variation in pooled oil composition which results from processes such as sulphurization, deasphalting, water-washing and biodegradation, whose effects are not solely temperature dependent.

oil families using gravimetric, chromatographic and particularly the carbon and sulphur isotope analyses of oils, oil fractions, and associated and non-associated natural gases.

b) Geologic Setting

To achieve the above objectives, an applicable field location with adequate sampling is necessary.

The oil and gas bearing reefs of the Upper Devonian Leduc Formation in central Alberta were well suited to this study. Three distinct hydrodynamic systems, which contain oils and gases with contrasting compositions, can be defined within the Leduc reservoir (see Hitchon, 1969a, 1969b). Oil in the Homeglen-Rimbey-Redwater system is generally low in sulphur, has a variable (generally high) API gravity, is saturated with gas and has associated gases low in hydrogen sulphide. In contrast, the oil in the other two hydrodynamic systems (the Wimborne-Duhamel and Stettler-West Drumheller trends) has generally much higher sulphur contents and its associated gas contains an abundance of hydrogen sulphide. The three hydrodynamic systems extend down dip and therefore have pools subjected to a range of reservoir temperatures (60° to 90°C). All of the pools in the three hydrodynamic systems contain mature hydrocarbons. However, individual Leduc pools at Harmattan, Strachan, Ricinus, Pine Creek, and Pine Northwest contain overmature dry sour gases. Gussow (1954) documented the process of gas displacement in the Rimbey-Meadowbrook Leduc reef trend. Consequently, the bulk composition and stable isotope content of Leduc oils and gases may be affected not only by maturation and sulphurization, but also by migration and gas deasphalting (see Evans _et al_., 1971).

Road access to the wellheads of the Leduc pools was excellent, and the majority of the pools were still on production. This facilitated sample acquisition. A vast amount of data has been collected on the hydrocarbon and formation water composition; on pool physical properties such as pressure, temperature and depth; and on pool areas and hydrocarbon reserves in the Leduc system. This information is easily accessible in the files of the Energy Resources Conservation Board in Calgary, Alberta. A portion of this data is published in summaries by White (1960), Century (1966) and Larson (1969). Furthermore, the geology of the Leduc system is well known (see McCrossan and Glaister, 1964).

Oil and associated gas samples were also taken from Keg River reefs at the Rainbow and Zama fields in Northwestern Alberta. The source of the hydrocarbons and sulphur for the Middle Devonian Keg River pools was believed to be different from the Leduc system. Therefore the use of oil composition data and the stable isotope values of oils, oil fractions and gas components to correlate between oils and oil families could be assessed.

c) Required Analytical Procedures

To meet the research objectives, a large number of analyses were necessary. The traditional method of hydrocarbon oxidation to carbon dioxide[+] (for carbon isotope analysis) is lengthy (a time in excess of 2 hours per oxidation is required) and is therefore not suited to batch sample processing. Alternate hydrocarbon oxidation methods have been described by Calvin *et al*. (1949) which were adapted in this thesis to stable isotope procedures to routinely process large numbers of samples.

The methane, ethane and propane natural gas components were required for isotope analysis. Therefore, a chromatograph-combustion system had to be designed to separate relatively large natural gas samples into their paraffin homologs and combust these, in sequence, to carbon dioxide and water. In order to minimize the time taken to run each gas sample, the capacity of the system had to be optimized so that generally one run per gas

---

[+] This method utilizes a copper oxide furnace and Toepler pump circulation system (refer to Craig, 1953 and Stahl, 1967).

sample would be required to generate enough carbon dioxide for the carbon isotope analysis of the methane, ethane and propane components.

Those analytical methods specifically devised and adapted to meet the needs of this research are described for the reader in Part I of this thesis. Other more standard procedures are only briefly described, but referenced, in Part I in order to provide the background for a discussion on the accuracy and reproducibility of the data derived using these methods. The formulae for the reagents used are listed in the appendix.

d) Coda

Over the rather lengthy period which this thesis has extended (1970 to 1978) aspects of its original objectives have been published by other researchers (see Orr, 1974; Orr, 1975; Hitchon et al., 1975 and Krouse, 1977). However, my interpretation of these "common objectives" is different, and in some cases the documentation is more detailed than in the published literature.

PART I

ANALYTICAL PROCEDURES, EXPERIMENTAL ERROR AND MASS SPECTROMETER CALIBRATIONS

CHAPTER I

EXPERIMENTAL PROCEDURES, ANALYSIS OF ERROR AND RELEVANT DISCUSSIONS

Section 1: Gas, Oil and Water Sampling Procedures

Co-produced gas, oil and water samples were taken at wellhead in 0.5 litre 1800 psig stainless steel sample bombs. Gas was transferred from the sample bombs to specially made 300 ml glass storage containers (see Figure I-1) using the apparatus shown in Figure I-2. Reactive sulphides in the gas were sampled using a cadmium acetate trap. Oil and water samples were poured from the sample bombs into 125 ml flasks, capped with parafilm, and stored under refrigeration.

The gas transfer procedure was rapid and required no elaborate apparatus (see Figure I-2). A 2-inch long, 1/4-inch O.D. piece of aluminum tubing was connected to the sample bomb using a 1/4-inch Swagelock fitting. The gas storage container was then pumped to high vacuum (pressures of less than 10^{-4} torr) flamed out and the two-way stopcock rotated from the AC to the BC flow position (see Figure I-3). One end of a short piece of tygon tubing was then attached to the aluminum tube and the other end to the "C" outlet of the two-way stopcock. A second piece of tygon tubing was then used to attach the "B" outlet to an L-shaped 8 mm

FIGURE I - 1

GAS STORAGE CONTAINER

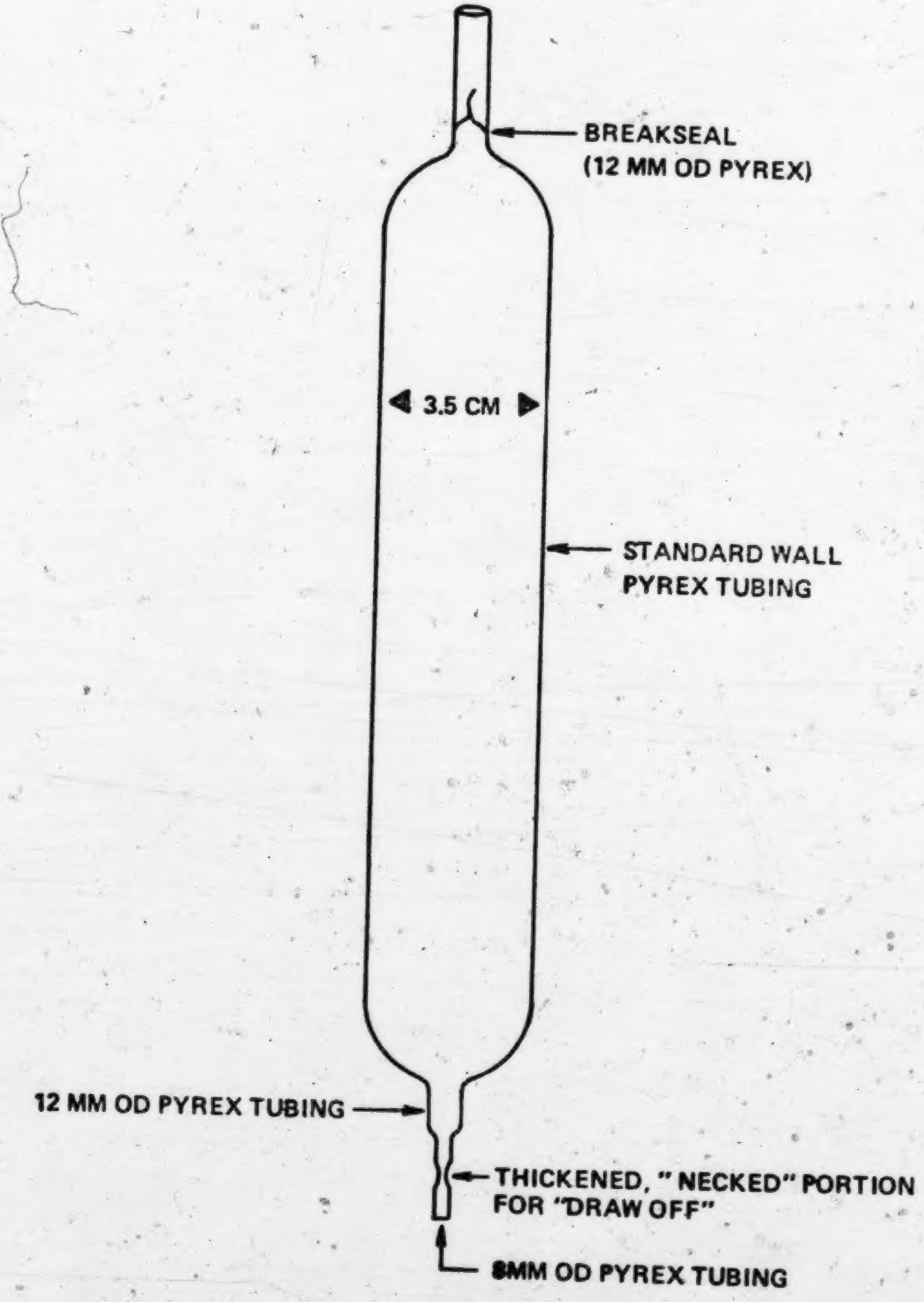

BREAKSEAL
(12 MM OD PYREX)
3.5 CM
STANDARD WALL
PYREX TUBING
12 MM OD PYREX TUBING
THICKENED, " NECKED" PORTION
FOR "DRAW OFF"
8MM OD PYREX TUBING

FIGURE I - 2

GAS SAMPLE TRANSFER APPARATUS

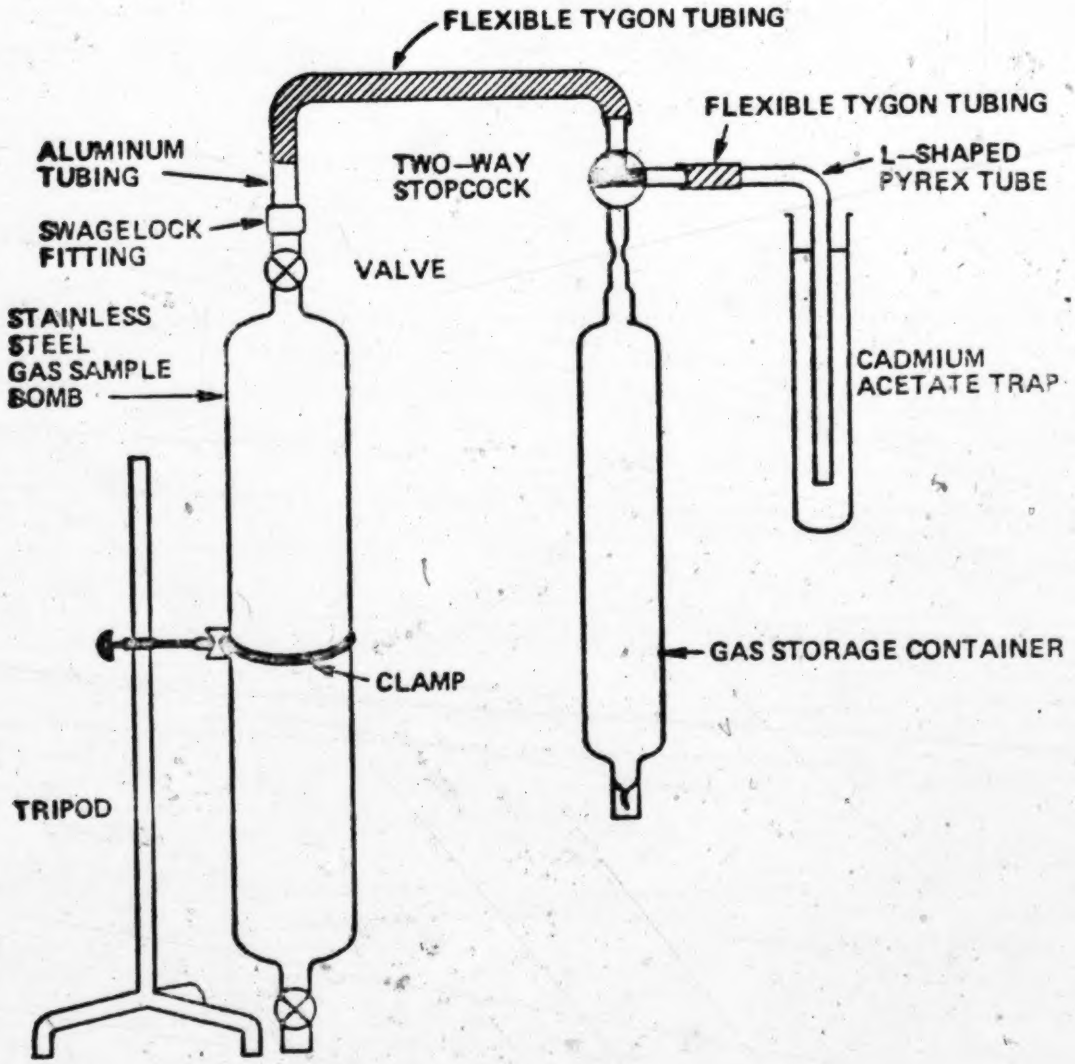
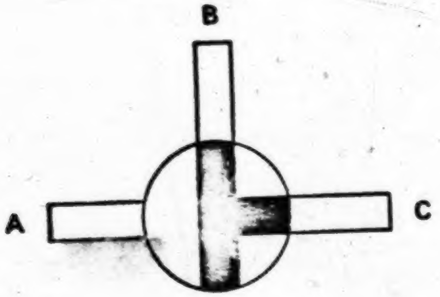
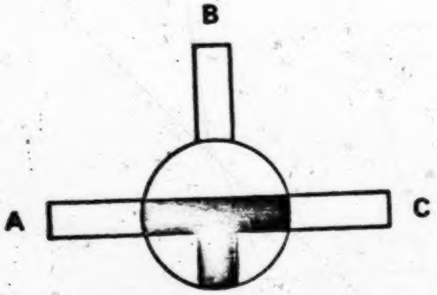

FLEXIBLE TYGON TUBING
FLEXIBLE TYGON TUBING
ALUMINUM TUBING
TWO—WAY STOPCOCK
L—SHAPED PYREX TUBE
SWAGELOCK FITTING
VALVE
STAINLESS STEEL GAS SAMPLE BOMB
CADMIUM ACETATE TRAP
GAS STORAGE CONTAINER
CLAMP
TRIPOD

FIGURE I - 3

STOPCOCK FLOW POSITIONS

BC FLOW POSITION





AC FLOW POSITION

O.D. glass tube which was then submerged in a 3 cm by 20 cm test-tube containing 0.15 M cadmium acetate solution. The natural gas was then bubbled through the cadmium acetate trap at a slow even rate of about one bubble per second. During this period, the gas transfer line was flushed of any air. When a time of three minutes had elapsed or a cadmium sulphide precipitate had formed which was equivalent to 40 to 200 mg of silver sulphide, the cadmium acetate trap was removed from the flow path by disconnecting the tygon tubing at the "B" outlet of the two-way stopcock. The gas flow rate was then increased and the two-way stopcock rotated to the AC flow position. The gas container was then filled until the pressure buildup caused leakage around the tygon-aluminum seal. At this point, the two-way stopcock was rotated to the BC flow position and the storage container removed from the transfer apparatus. The remainder of the gas in the sample bomb was exhausted to atmosphere in the fume cabinet. When the pressure in the sample bomb reached atmospheric values, the liquid contents were poured into 125 ml erlenmeyer flasks and stored under refrigeration. During the liquids' transfer period, the gas storage container was cooled in a dewar of liquid nitrogen. At liquid nitrogen temperatures the vapour pressure of methane and ethane was so low that the two-way stopcock could be drawn off the sample container using an oxymethane torch without causing any reaction of the sample at the heated glass surface. Once the stopcock was drawn off, the gas storage container became a perfectly sealed vessel in which the gas sample could be stored indefinitely and remain uncontaminated. The gas sample could be removed for analysis by breaking the glass seal at the end of the container.

Section 2: Extraction of Sulphur Compounds From Natural Gases and Formation Waters

a) Recovery of Sulphides From Natural Gases

Reactive sulphides such as hydrogen sulphide, polysulphides, thiols, and some organic mono and disulphides were extracted as a group from natural gases by bubbling the sour gas through a 0.15 M cadmium acetate solution. The experimental apparatus and techniques used are described in Chapter I, Section 5 and Chapter I, Section 3. For natural gases in which the hydrogen sulphide component was abundant enough, this sulphide was recovered using chromatographic procedures outlined in Chapter I, Section 5.

Gaseous and vapour phase organic mono and disulphides and thiols contribute an uncertain, but generally considered to be small, sulphide content to an associated gas. For example, Vredenburgh and Cheney (1971) report an abundance of 15 grains per 100 SCF of combined thiol, alkyl sulphide, carbon disulphide and carbonyl sulphide, as compared to a hydrogen sulphide content of 3 to 4% for some associated Wind River Basin gases. However, it is highly probable that, depending on factors such as the presence of native sulphur in the reservoir, formation temperature and pressure, wellhead temperature and pressure, and the abundance of the C_5 component in the natural gas, hydrogen sulphide together with an abundance of coexisting polysulphides could be sampled at the wellhead (Hyne, 1968 and Muller and Hyne, 1969). Further, the isotope composition of these gaseous sulphides, possible reactions that cause sulphur isotope fractionation between these compounds, the variation of this isotope fractionation with temperature, and the factors which control the abundance of these sulphides are not known. Therefore, it was necessary to establish the validity of the commonly used assumption (refer to Thode et al. 1958; Vredenburgh and Cheney, 1971; Hitchon et al. 1975 and Orr, 1974) that the sulphur isotope composition of the total sulphide precipitate, collected from a natural gas using cadmium acetate solution, was equivalent to the sulphur isotope composition of the hydrogen sulphide component. In Table I-I is a comparison of the sulphur isotope composition of the total sulphide precipitate and the chromatographed hydrogen sulphide component from several gas and oil pools in Alberta. For the non-associated gases (refer to Levorsen, 1967) in Table I-I, the sulphur isotope composition of the hydrogen sulphide gas is the same, within error, as the sulphur isotope composition of the total sulphide precipitate. This implies that either hydrogen sulphide is the only reactive sulphide of any abundance in the gas phase or that the gaseous phase sulphides in these natural gases have the same sulphur isotope composition. For the associated gases (refer to Levorsen, 1967) from Buffalo Lake and Bashaw D-3 pools, the difference in sulphur isotope composition of the hydrogen sulphide gas and the total sulphide precipitate, respectively 0.7‰ and 1.1‰ is significantly larger than error. This im-

TABLE I-I

COMPARISON OF SULPHUR ISOTOPE VALUES FOR CHROMATOGRAPHED HYDROGEN SULPHIDES AND TOTAL SULPHIDE PRECIPITATES FROM NATURAL GASES

Sample Description	δS^{34} Chromatographed H_2S	δS^{34} Total Sulphide Precipitate	Type of Gas
Ricinus 7-13-36-10 W5M	+20.4‰	+20.3‰	non-associated
Ricinus 10-33-36-10 W5M	+20.4‰	+20.4‰	non-associated
Pine Northwest (HBOG, Separator)	+23.0‰	+23.0‰	non-associated
Pine Creek 10-16-58-19 W5M	+22.2‰	+22.2‰	non-associated
Pine Creek 10-23-57-19 W5M	+22.0‰	+22.2‰	non-associated
Pincher Creek PC-73-61 (GOC)	+15.7‰	+15.8‰	non-associated
Harmatten 10-11-32-3 W6M	+22.4‰	+22.6‰	non-associated
Wimborne (Aggregate sample from wells 4-1-33-26 W4M and 7-26-33-26 W4M)	+16.3‰	+16.3‰	associated
Erskine 8-26-39-21 W4M	+15.1‰	+15.2‰	associated
Clive (Aggregate sample from wells 16-29-40-24 W4M and 12-35-39-21 W4M)	+15.5‰	+15.7‰	associated
Buffalo Lake 4-35-39-21 W4M	+14.7‰	+15.4‰	associated
Bashaw 10-6-42-22 W4M	+14.7‰	+15.8‰	associated

plies that there may be a significant content of organic sulphide compounds or polysulphides within the solution gas phase from these two pools. The fact that associated gases from Wimborne, Erskine and Clive have very similar sulphur isotope values for hydrogen sulphide gas and total sulphide precipitate indicates that a sour gas in association with a sulphurous oil phase is not the sole criterion for incorporating isotopically dissimilar sulphides into the solution gas phase. Therefore, inferences regarding the reservoir sulphur system from the sulphur isotope composition of the total sulphide precipitate from solution gases must recognize that this del value is not necesarily equivalent to the del value of the hydrogen sulphide component of the natural gas. These del values may differ by 1 per mil or more. Also, the total sulphide precipitate sulphur isotope values from associated and non-associated gases may not be readily comparable.

b) Recovery of Sulphur Compounds From Formation Water

Water was decanted from oil and solution gas samples from Bashaw, New Norway and Erskine and from gas samples from Pine Creek, Beaver River and Sylvan Lake. Each water sample was stored in one or more 125 ml Erlenmeyer flasks and capped with parafilm.

During and after the recovery of the water samples from the gas bombs from Pine Creek, Beaver River and Sylvan Lake, a rapid outgassing of sour natural gas was observed, as well as the formation of a yellow-green crystalline crust at the water-air interface. None of the waters from these three wells showed any Tyndall effect, indicating a fine suspension of native sulphur. After the water samples stopped out-gassing, a 10 ml aliquot was taken from each and mixed with 1 ml of 0.15 M cadmium acetate solution. No yellow-orange cadmium sulphide precipitate was observed to form in either the Pine Creek or Beaver River water samples. Dissolved sulphide was recovered from the Sylvan Lake sample by adding two successive 10 ml aliquots of 0.15 M cadmium acetate solution to a 250 ml sample of water. After the addition of each aliquot of cadmium acetate solution, the sulphide precipitate[+] was allowed to settle and the cadmium-sulphide-free water was decanted off. Little further CdS was precipitated on the addition of the second 10 ml aliquot. Around 150 ml of sulphide-precipitate-free water was decanted off for sulphate ion recovery. No attempts were made to vary the Eh or pH of the water samples to try and extract any more sulphides than could be precipitated from a combination of 1 ml of 0.15 M cadmium acetate solution in 10 ml of water or 10 ml of cadmium acetate solution in 250 ml of water followed by another 10 ml aliquot in roughly 200 ml of water. A 125 ml aliquot of water was taken from each of the three water samples from Sylvan Lake (processed water), Beaver River and Pine Creek and placed in a 250 ml beaker, capped with parafilm, in preparation for sulphate ion recovery.

[+] This precipitate may contain a minor amount of $CdSO_4$.

The yellow-green crystalline crust was removed from the surface of the Beaver River, Sylvan Lake and Pine Creek water samples and washed in a coarse filter paper with n-pentane. This washing procedure removed a film of hydrocarbon that made preparation of the crust for x-ray analysis quite difficult. A portion of the crust was then placed in an extract thimble and was continuously washed with insecticide grade benzene in a soxhlet apparatus for a 24-hour period. The crystals that remained in the extract thimble were x-rayed and identified as calcite and quartz. No sulphates were detected. The benzene in the soxhlet reservoir was evaporated at low heat and clear yellow crystals with a prismatic habit were recovered. These were x-rayed and identified as native sulphur and stored for sulphur isotope analysis.

Water samples taken from Erskine, Bashaw and New Norway D-3 reservoirs all showed a pronounced Tyndall effect. Only the 10 ml aliquot from Erskine gave a cadmium sulphide precipitate. No crystalline crust formed on these three water samples. The colloidal suspensions in the Bashaw and New Norway waters remained stable throughout the period of time allotted for water sulphate recovery and the samples were therefore not analysed. The colloids were suspected to be native sulphur since the water had a sulphurous odor, a very light milky colour, and the minute amount of flocked substance from the Erskine sample had a light yellow colour. These waters appeared to be saturated with native sulphur and could be involved with the following reactions suggested by Berner (1963):

$$H_2S \longrightarrow HS^- + H^+$$

$$HS^- \longrightarrow H^+ + S^{-2}$$

$$S^{-2} \longrightarrow S^\circ + 2e^-$$

The polysulphide reaction suggested by Hyne (1968) may also be involved. That is:

$$H_2S_{x+1} \longrightarrow H_2S + S_x^\circ$$

The products from the dissociation of the polysulphide could then participate in the aqueous reactions proposed by Berner (1963). Another cause for the formation of native sulphur in the crystalline crust could be the oxidation of the out-gassed hydrogen sulphide by air oxygen at the air-water interface.

The procedure used for sulphate ion recovery was essentially that described by Maxwell (1968). Several points about the procedure are worth noting. Prior to the beginning of the chemical treatment of the 125 ml aliquot of water, it was filtered through a white Schleicher and Schuell filter paper into a 400 ml beaker. The filter paper was then washed 12 times with distilled water. This procedure removed any solids from the water sample. Methyl orange indicator was then added to the solution and it was acidified with concentrated hydrochloric acid and then heated until all effervescence stopped. This procedure not only removed bicarbonate and carbonate ions and their complexes, but also removed any aqueous hydrogen sulphide and bi-sulphide ions. Rather than retain iron or other common transition metals in solution in their reduced state or as a citrate complex, they were removed as their insoluble hydroxides using an excess of concentrated ammonium hydroxide. The sulphate ion was precipitated by bringing the acidified solution to a boil and adding two 20 ml aliquots of 2-1/2% barium chloride solution. After the addition of each aliquot of barium ion, the boiling solution was stirred vigorously for two minutes. The barium sulphate precipitate was let stand over night prior to its recovery by filtration. These last two procedures produced reasonable coarse barium sulphate crystals and therefore more accurate sulphate analyses.

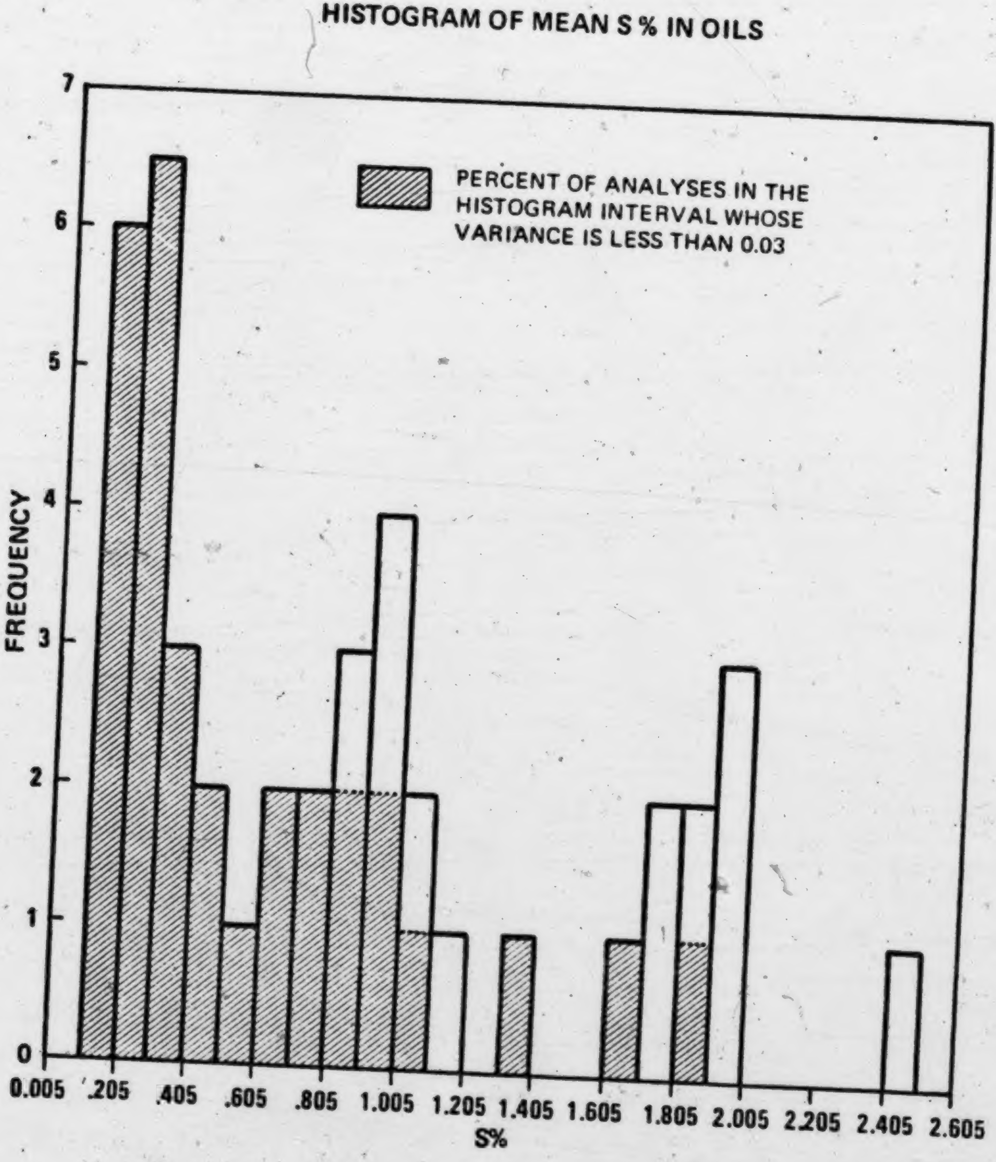
Section 3: Extraction of Oil Sulphur and Its Preparation for Isotope Analysis

a) Total Sulphur Extraction From Oils

Sulphur was quantitatively extracted from H_2S - free oils using the technique outlined in the Parr Oxygen Bomb instruction manual No. 130 published by the Parr Instrument Company, Moline, Illinois. In this method, a 0.7 to 0.9 gm oil sample was explosively combusted in 25 to 27 atm. of oxygen gas. All sulphur compounds within the oils were oxidized to sulphate and recovered as $BaSO_4$ using a 2% to 5% $BaCl_2$ solution. Procedures for quantitative recovery of the sulphate ion using the barium sulphate method are described by Maxwell (1968).

The reproducibility of sulphur percents determined using this method was calculated as the variance of replicate analyses. For sulphur percents with 3 or fewer analyses, the variance was estimated by assuming normality and multiplying the range by an appropriate constant (see Dixon and Massey, 1969). Reproducibility was excellent, but it was a function of per cent sulphur. The histogram in Figure I-4 shows that two populations of mean sulphur percents can be defined by noting the fraction of sulphur percents per histogram interval whose variance is less than or equal to 0.03. The variance of the two populations so defined is substantially different.

FIGURE I - 4


HISTOGRAM OF MEAN S % IN OILS
PERCENT OF ANALYSES IN THE HISTOGRAM INTERVAL WHOSE VARIANCE IS LESS THAN 0.03
FREQUENCY
0
1
2
3
4
5
6
7
0.005
.205
.405
.605
.805
1.005
1.205
1.405
1.605
1.805
2.005
2.205
2.405
2.605
S%

The reproducibility of any total sulphur analysis whose sulphur value is in the range of 0.10 to 0.90 percent inclusive is roughly the same, but different from the common variance of any analysis whose sulphur value exceeds 0.90 per cent. These two variances can be estimated using a pooling technique outlined by Johnson and Leone (1964). The standard deviation associated with any sulphur analysis whose sulphur percent lies within the range 0.10 to 0.90 inclusive is 0.01. The standard deviation for analyses whose sulphur percents exceed 0.90 was calculated to be 0.06.

b) Conversion of Sulphate to Silver Sulphide

Barium sulphate obtained from the Parr Bomb combustion of crude oils was converted to Ag_2S using a wet reduction procedure. The silver sulphide was then recovered and stored to be burned to sulphur dioxide for sulphur isotope analysis.

In the reduction procedure around 50 mg of barium sulphate was reduced to hydrogen sulphide by boiling the sulphate with 50 ml of a solution consisting of HI (SG=1.7), concentrated HCl and H_3PO_2 (50%) mixed in volumetric proportions of 2.039 HI:3.328 HCL:1 H_3PO_2. The reduction was carried out in a 200 ml round bottom flask which was connected to a nitrogen flow line in series with a reflux condenser, a distilled water scrubber and a cadmium acetate solution adsorber. During the boiling, HCl, HI and H_3PO_2 vapours were returned to the round bottom flask by condensation and gravity fall along the sides of the reflux condenser. Any reagents which escaped from the reflux condenser were removed from the gas flow by the distilled water scrubber. Therefore, the product hydrogen sulphide was carried through the system in a flow of nitrogen to the cadmium acetate trap where it was quantitatively precipitated as a bright yellow orange sulphide free from reducing solution contamination. The H_2S-free nitrogen was exhausted to the atmosphere. A time of 90 minutes was adequate to reduce all sulphate to hydrogen sulphide and precipitate this as cadmium sulphide. This time period was, however, dependent on the nitrogen carrier gas flow rate and the grain size of the barium sulphate. Finer grain sizes resulted in faster dissolution rates and shorter reaction times. An optimum flow rate of one bubble per second was found. This flow rate results in a bright yellow-orange CdS precipitate. Dark orange colours indicate a much too slow flushing rate.

The sulphate reduction reaction is reasonably complex with the reduction of sulphate to hydrogen sulphide probably being a first order reaction (C. E. Rees, personal communication). Hydriodic acid is the active reducing agent, converting SO_4^{-2} ions to H_2S and itself in turn being oxidized to free iodine. The hypophosphorous acid reacts with the free iodine converting it back to I^{-2} which can rereact with SO_4^{-2} ions. Hydrochloric acid acts as a solvent for sulphate ions and a source for hydrogen ions.

By titrating the cadmium sulphide precipitate with a 0.5 N silver nitrate solution and boiling the mixture, the original fine-grained precipitate was converted to an easily-filterable, coarse-grained silver sulphide curd. The silver sulphide was recovered using a fine or medium sintered glass vacuum filter. During the filtration, the Ag_2S was washed with concentrated NH_4OH to remove any contaminant AgCl and then washed several times with distilled water. The relatively pure silver sulphide was then dried in its filter crucible at 100°C to 120°C for a period of an hour or so. Specifications for the reagents used in this reduction procedure can be found in Appendix I. Further description of the reduction procedure can be found in Harrison and Thode (1957) and Pepkowitz and Shirley (1951).

Yields ($\frac{\text{gms reduced S}}{\text{gms oxidised S}}$ x 100) were generally much less than 100% and ranged from 80% to 95% with a mode at 89% and a mean at 88% (see Figure I-5). Such variable yields did not affect the sulphur isotope value of the sulphide or sulphate outside of the mass spectrometer analytical error, which is $\pm 0.2‰$. This statement can be supported by referring to Table I-II. The calculated standard deviation of the five replicate sulphur analyses of the barium sulphate laboratory standard is 0.1‰. Though the yields range from 84% to 95%, the error in the sulphur isotope analyses of the standards is not greater than that produced by the mass spectrometer. The sulphur isotope composition of the lead sulphide laboratory standards (see Table I-II) further emphasizes this point. In the

FIGURE I - 5

YIELD HISTOGRAM FOR THE SULPHATE REDUCTION LINE

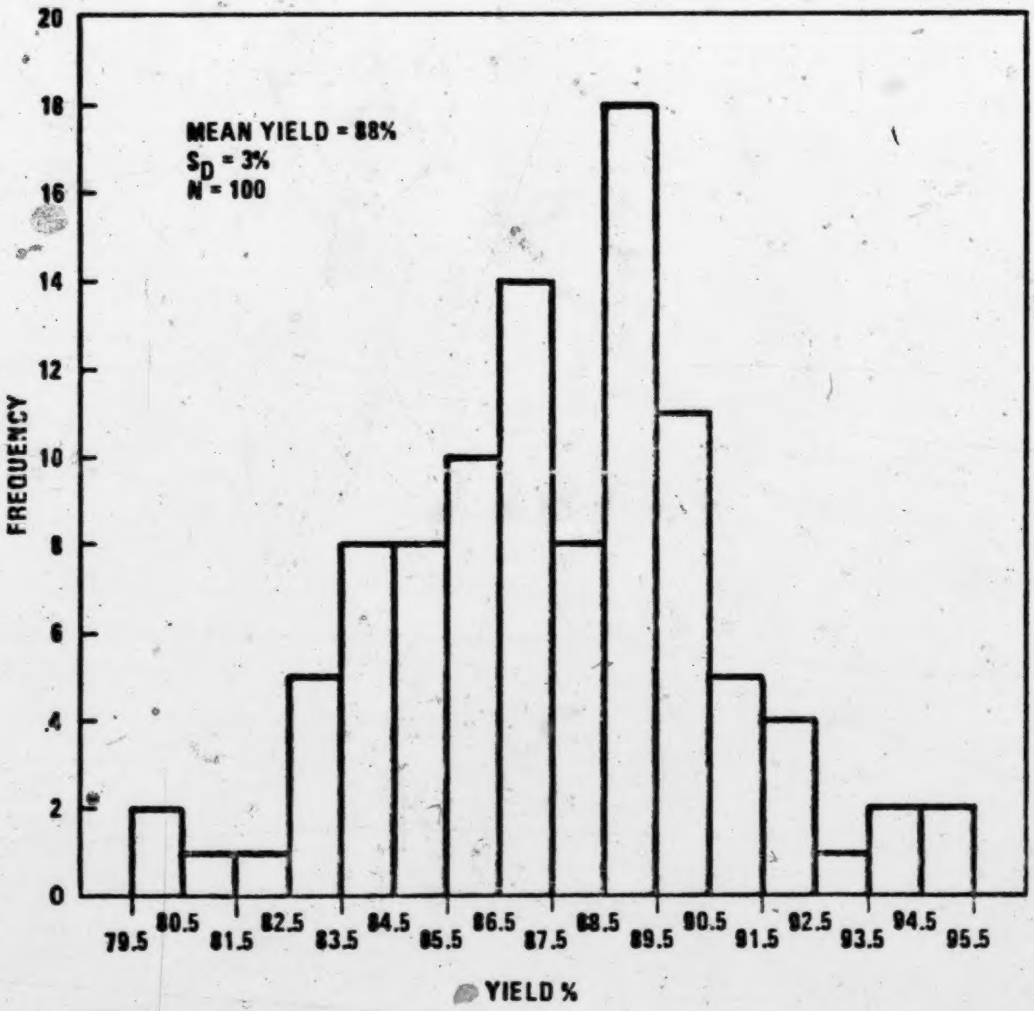


TABLE I-II

YIELDS AND SULPHUR ISOTOPE ANALYSES FOR REPLICATE SULPHATE AND SULPHIDE REDUCTIONS

Sample Description	Sample Preparation	Reduction Line Yield	SO_2 Burn Yields	S^{34}_{CDT}
$BaSO_4$ Lab. Standard	Reduced to Ag_2S	95%	100%	+2.5‰
$BaSO_4$ Lab. Standard	Reduced to Ag_2S	85%	100%	+2.8‰
$BaSO_4$ Lab. Standard	Reduced to Ag_2S	84%	100%	+2.6‰
$BaSO_4$ Lab. Standard	Reduced to Ag_2S	90%	100%	+2.6‰
$BaSO_4$ Lab. Standard	Reduced to Ag_2S	89%	100%	+2.7‰
PbS Lab. Standard	Reduced to Ag_2S	82%	100%	-5.8‰
PbS Lab. Standard	Burned directly to SO_2	N.A.	99%	-5.7‰

first analysis the PbS standard was converted to silver sulphide and this then burned to SO_2. In the second analysis, a sample of the PbS standard was burned directly to sulphur dioxide leaving out the intermediate reduction step. The del. values of both lead sulphide samples agree within the error of the mass spectrometer despite the 17% difference in conversion yields.

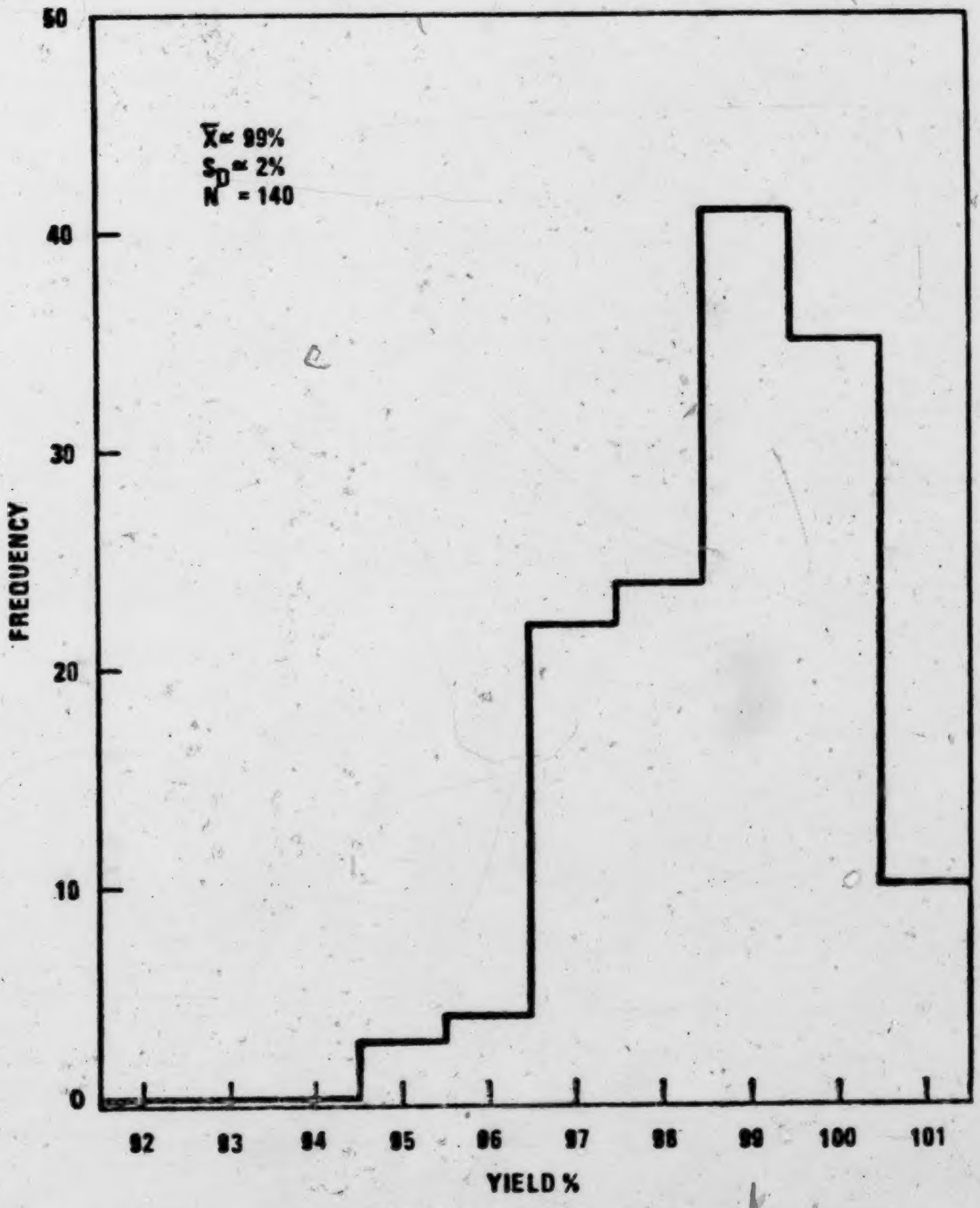
c) Conversion of Silver Sulphide to SO_2

Silver sulphide, obtained from the wet reduction of sulphate was converted to SO_2 using the copper oxide method. This method has been discussed by Fritz et al. (1973) and Robinson and Kusakabi (1975). Generally, 0.042 gm of Ag_2S were intimately mixed with 0.1000 gm of purified red copper oxide by gently grinding both together in a quartz mortar. The weights of oxidant and sulphide were chosen to assure a molar oxygen to sulphur ratio of not less than 4:1 and not more than 5:1. The cuprous oxide was purified by heating it to 500°C under high vacuum for a period of 24 hours. The cuprous oxide and silver sulphide mixture was loaded into a 1-1/2 cm x 9 mm silica glass cylinder and contained by loosely plugging both ends of the cylinder with quartz glass wool. The loaded cylinder was then placed inside of a quartz glass combustion tube and the silver sulphide oxidized to SO_2 under vacuum at temperatures in excess of 1000°C for a period of 20 minutes. A mixture of O_2, CO_2, H_2O, and SO_2 was obtained from the combustion. Water was removed from the gas mixture during combustion by freezing CO_2 and SO_2 through an acetone-dry-ice cold trap to a cold finger at liquid nitrogen temperatures. Oxygen was removed by pumping the system to high vacuum after the combustion was over and all the CO_2 and SO_2 were frozen down into the N_2 cold finger. Carbon dioxide was separated from sulphur dioxide by a vapour pressure distillation technique. The frozen mixture of CO_2 and SO_2 was warmed to the temperature of a n-pentane liquid-crystal slush. This slush was prepared by mixing n-pentane and liquid nitrogen in a dewar. At this temperature, -132°C, sulphur dioxide has a very low vapour pressure (10^{-16} mm Hg) while carbon dioxide has an appreciably higher vapour pressure (1 mm Hg). Therefore, the CO_2 can be removed by freezing it over into an evacuated cold finger at N_2 temperatures without removing a significant amount of the SO_2. The purified sulphur dioxide was then freeze-transferred to a mercury manometer where the number of moles of gas was measured. The gas was then transferred to a glass breakseal container for storage.

According to J. Monster (personal communication) and Fritz et al. (1973), silver sulphide is the easiest sulphide to burn and the combustion yields, that is, $\frac{\text{gms } SO_2 \text{ sulphur}}{\text{gms sulphide sulphur}} \times 100$, are constantly close to 100%. Figure I-6 is a histogram of yields. For

FIGURE I - 6

HISTOGRAM Ag_2S – COPPER OXIDE BURN YIELDS



the 140 sulphides combusted, the mean yield is 99% and the standard deviation approximately 2%. An analysis of Fritz _et al_'s 1973 data shows that replicate isotope analyses of a silver sulphide standard, burned with an excess of oxidant over a range of temperatures from 800°C to 1100°C and with a range of yields of 94% to 104%, agreed within the error of the mass spectrometer, which is ±0.2‰. Therefore, no significant error in sulphur isotope analysis is expected from the observed variation in burn yields.

Section 4: Oxidation of Oils for Carbon Isotope Analysis

a) Introduction

Oils and their saturate and aromatic fractions were oxidized to carbon dioxide and water using a wet oxidation procedure and a Carius tube-cupric oxide technique. The basic concepts for these two methods are outlined in a book by Calvin _et_ _al_. (1949). These concepts were adapted to stable isotope preparation and extraction procedures and the two oxidation techniques were devised as alternates to the high temperature copper oxide combustion furnace method for the oxidation of liquid hydrocarbons. Descriptions of the copper oxide combustion furnace method can be found in Stahl (1967) and Craig (1953). Carbon isotope analyses of interlaboratory oil standards and NBS oil standard No. 22, oxidized using the Carius tube and wet oxidation procedures, agree within error with the δC^{13}+ analyses of these same standards oxidized by the more commonly used copper oxide furnace method. δC^{13} values for carbon dioxides derived from both the Carius tube-cupric oxide and wet oxidation methods have an associated 1σ error of 0.2‰.

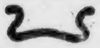
+ $$\delta C^{13} = \left(\frac{\frac{C^{13}}{C^{12}}\ \text{Sample}}{\frac{C^{13}}{C^{12}}\ \text{Standard}} - 1 \right) 1000\ ‰$$

b) Wet Oxidation Procedure

The wet oxidation procedure was designed for the low temperature oxidation of crude oils, tars, pyrobitumens, and natural gases. In this method about 3 mg of oil or hydrocarbon equivalent was weighed out in a specially made glass button (see Figure I-7). The glass button and contained oil were then carefully dropped to the base of the main chamber of a K-shaped reaction vessel (see Figure I-8). The side arm portion of the reaction vessel was then partially filled with 3 to 5 ml of a modified Van Slyke-Folch oxidizing reagent (see Appendix I and Calvin et al. 1949). The reaction vessel was then attached to the vacuum line (see Figure I-9) by a reagent resistant teflon ultra torr union and the contained oil sample was frozen down using a dewar of liquid nitrogen. After a freezing period of 2 minutes, the reaction vessel was evacuated, first to a low vacuum and then to high vacuum. During this period the oxidizing solution continually outgassed. Evacuation was stopped when the reagent showed no visible signs of outgassing. This took approximately 15 to 30 minutes. Over this period, the liquid nitrogen dewar around the oil had to be continually topped up to avoid loss of the more volatile portion of the oil. After evacuation, the portion of the reaction vessel attached to the vacuum line was drawn off using an oxy-methane torch. Three to six oils could be processed simultaneously through this stage. Next, the reaction vessel was removed from the liquid nitrogen dewar and allowed to come to room temperature. The oxidizing solution was then tipped

FIGURE I-7

SIDE VIEW OF A GLASS BUTTON SAMPLE CONTAINER



WALLS ARE APPROXIMATELY
1-2 mm HIGH

5 mm DIAMETER

FIGURE I - 8

SIDE VIEW OF A K-FORM REACTION VESSEL

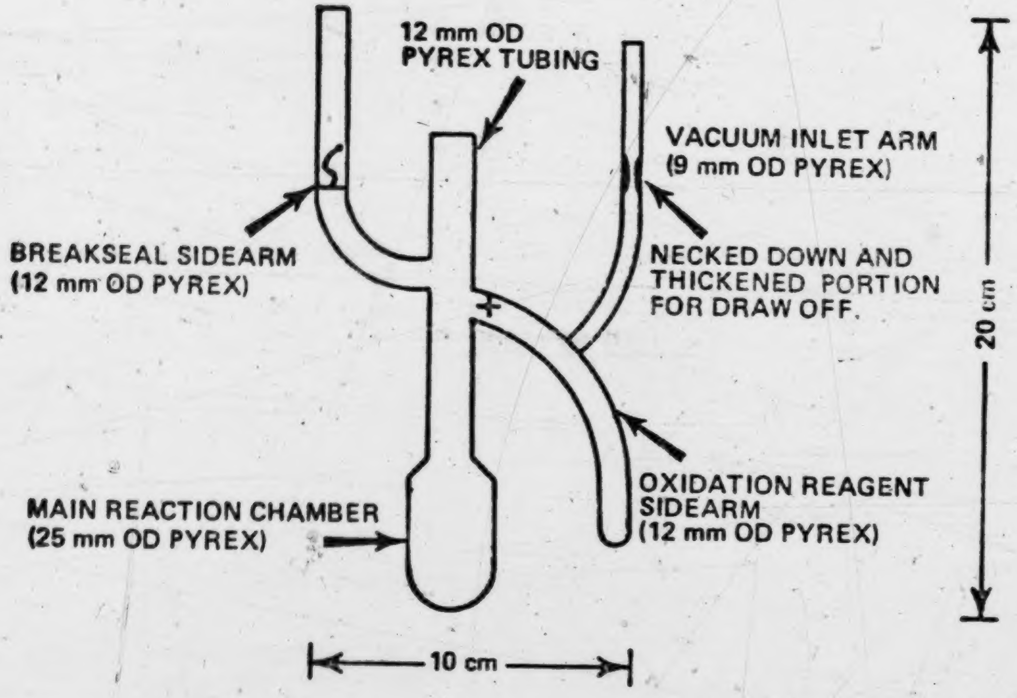
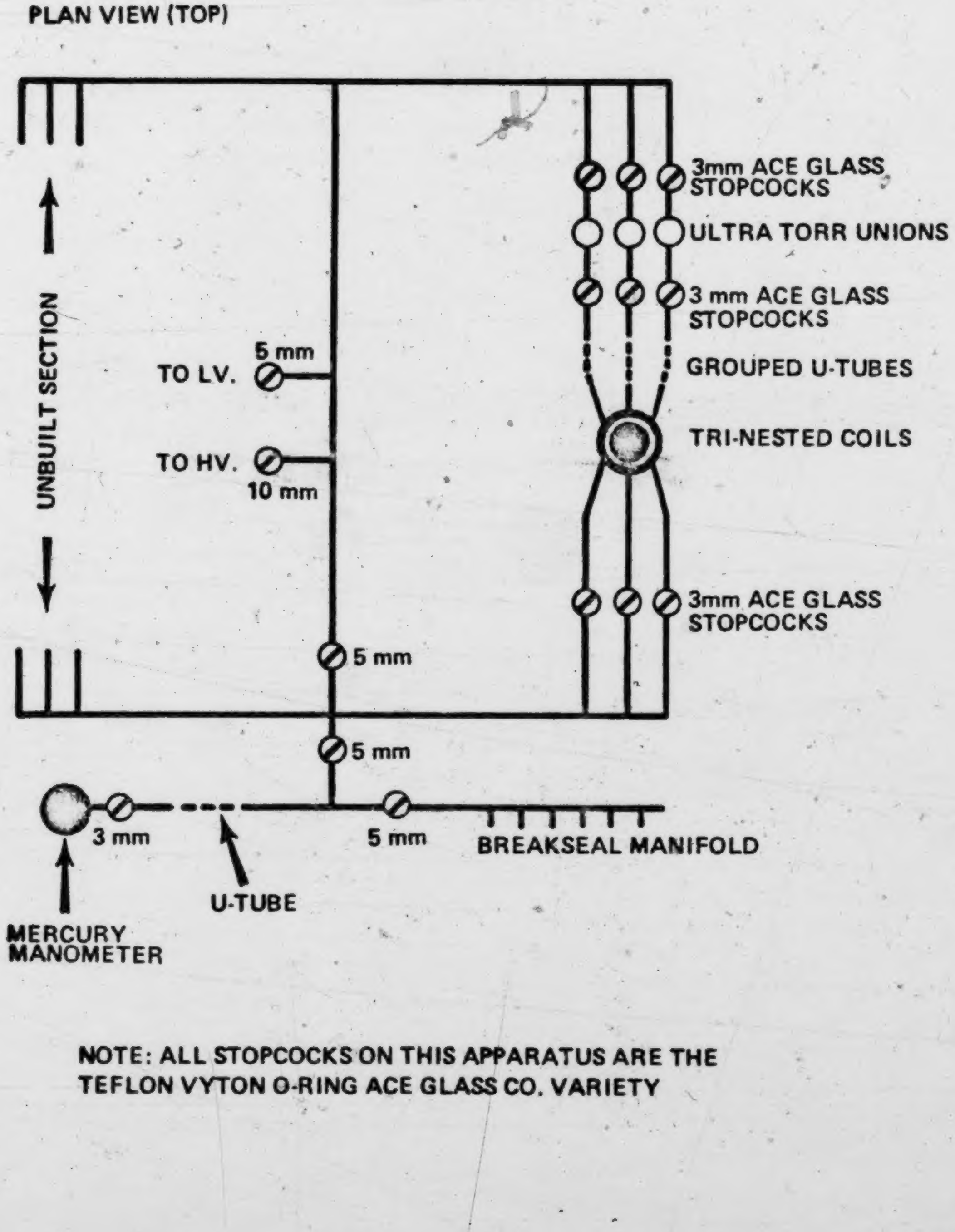

12 mm OD
PYREX TUBING
VACUUM INLET ARM
(9 mm OD PYREX)
BREAKSEAL SIDEARM
(12 mm OD PYREX)
NECKED DOWN AND
THICKENED PORTION
FOR DRAW OFF.
20 cm
OXIDATION REAGENT
SIDEARM
(12 mm OD PYREX)
MAIN REACTION CHAMBER
(25 mm OD PYREX)
10 cm

FIGURE I-9

VACUUM EXTRACTION AND PREPARATION APPARATUS

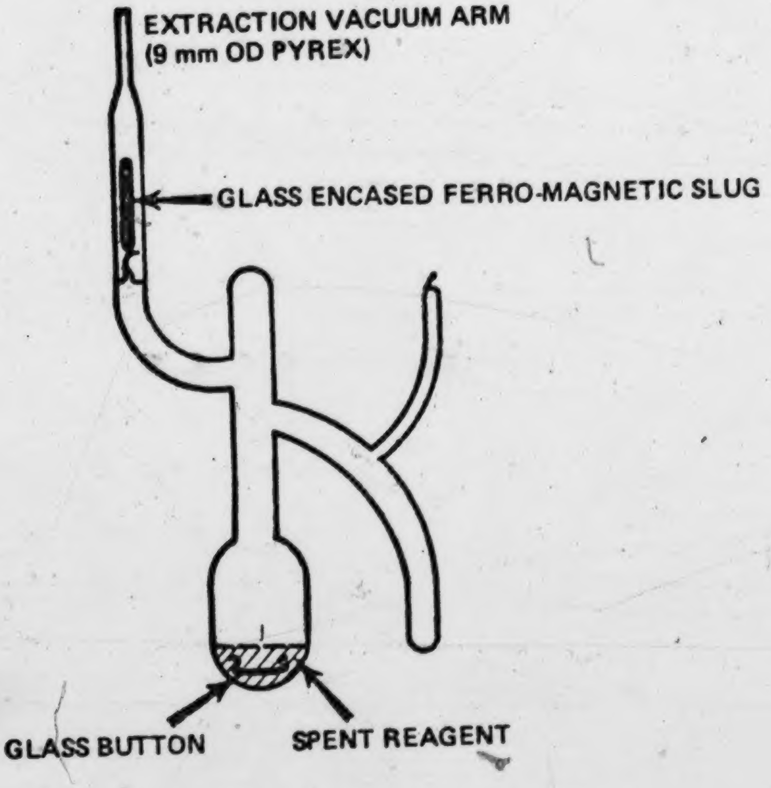

PLAN VIEW (TOP)
3mm ACE GLASS STOPCOCKS
ULTRA TORR UNIONS
3 mm ACE GLASS STOPCOCKS
GROUPED U-TUBES
TRI-NESTED COILS
3mm ACE GLASS STOPCOCKS
UNBUILT SECTION
5 mm
TO LV.
TO HV.
10 mm
5 mm
5 mm
3 mm
5 mm
BREAKSEAL MANIFOLD
U-TUBE
MERCURY MANOMETER

NOTE: ALL STOPCOCKS ON THIS APPARATUS ARE THE TEFLON VYTON O-RING ACE GLASS CO. VARIETY into the oil. Reaction of the reagent with the oil was immediate and quite rapid as the solution was gently heated and swirled over a bunsen flame. After a heating period of 2 to 5 minutes all reaction had ceased and the reagent took on a chromium III green colour. Since the reaction vessels were completely vacuum tight, they could be set aside until enough oil samples had been processed to warrant beginning the CO_2 extraction phase.

Twenty-four oil samples were oxidized before the carbon dioxides were extracted. The vacuum line illustrated in Figure I-9 was designed to extract and purify the carbon dioxides from three reaction vessels simultaneously. Provision was made in the apparatus to expand it to ultimately process the gases from six reaction vessels. Each reaction vessel was modified for extraction (see Figure I-10) and connected to the vacuum line using 1/4-inch teflon ultra torr unions. The entire line was then pumped down to a vacuum of less than 1×10^{-4} torr. The extraction portion of the line was then isolated, the seals on the three reaction vessels broken, and the carbon dioxide gases plus contaminants allowed to expand through a dry ice-acetone trap to a liquid nitrogen trap, where the carbon dioxide was frozen out. Any SO_3 (from the oxidizing solution) and water remained in the acetone-dry ice trap. After 5 minutes of freezing, the liquid nitrogen trap was topped up and the line was opened to low vacuum. Once a good low vacuum was reached, the reaction vessels were isolated from the extraction line and the line was then pumped to a high vacuum. At this point,

FIGURE I - 10

SIDE VIEW OF A K-FORM REACTION VESSEL MODIFIED FOR EXTRACTION


EXTRACTION VACUUM ARM
(9 mm OD PYREX)
GLASS ENCASED FERRO-MAGNETIC SLUG
GLASS BUTTON
SPENT REAGENT

oxygen produced from the oxidation reaction was removed. These two pumping periods totalled about ten minutes. Pumping for too long a time may cause isotope fractionation, as carbon dioxide has a finite, though small, vapour pressure at liquid nitrogen temperatures. The system was then isolated from the vacuum pumps and the liquid nitrogen dewar removed from the nested coils. These were then warmed to room temperature and then refrozen to liquid nitrogen temperatures. This step was necessary to remove any oxygen trapped in the solid CO_2 structure. Once refrozen, the solid carbon dioxide was briefly pumped to high vacuum. This pumping period was monitored on the vacuum gauge and little contaminant oxygen was detected. After this final purification step, the liquid nitrogen dewar was removed from around the nested coils and they were warmed to room temperature. Each of the three carbon dioxide samples were then freeze transferred in turn to a mercury manometer, where their STP volume was measured, and then transferred to a breakseal for storage.

The low temperature of the oxidation reaction, as well as the very powerful nature of the Van Slyke-Folch reagent, made it extremely improbable that any carbon monoxide was produced during the oxidation reaction. No water or sulphur dioxide was detected in several samples of the purified carbon dioxide gas scanned on the 12-inch gas source mass spectrometer. Nitrogen oxide impurities were not rigorously sought; however, using colour as a qualitative criterion, no N_2O_3, NO_2, N_2O_4, or NO_3 could be detected. Since any combined nitrogen should be retained in the sulphuric acid solution as ammonium sulphate, no nitrogen oxides should have been produced. Blank runs using only the oxidizing solution showed no extraneous carbon dioxide contamination.

Percentages of carbon in the oil samples were calculated from the STP volume measurements. A maximum possible relative error due to measurement uncertainties was calculated to be ±4%. Duplicate analyses of oil sample carbon percents and their δC^{13} values quoted to PDB are shown in Table I-III. Too great a difference in replicate carbon percentages such as in GOC Zama 12-21 (see Table I-III) indicates extraction and/or sample preparation error. This difference did not, however, affect the carbon isotope results. The pooled estimate of standard deviations (Johnson and Leone, 1964, and Dixon and Massey, 1969) calculated for the duplicate carbon percentages and δC^{13} values are, respectively, 2% and 0.2‰. A rigorous investigation of the accuracy of the quantitative carbon determination for oils was not done. However, Table I-IV lists carbon yields determined using the wet oxidation procedure for a non-volatile solid cadmium acetate ($Cd[CH_3COO]_2$). The mean yield was 92.1% and the associated standard deviation was 1.8%. The low yields are not surprising. As a rule, carbon dioxide is very difficult to remove from solution even in an acid medium. For example, low yields are a common occurrence in the phosphoric acid treatment of calcite for carbon isotope measurements of carbonates (Dr. D. C. Herrick, personal communication).

TABLE I-III

DUPLICATE CARBON PERCENTS AND δC^{13} VALUES
FOR OILS OXIDIZED USING THE WET OXIDATION METHOD

Sample Description	Carbon Percent	δC^{13}_{PDB}
IOE Big Lake 9-26	77.0% 76.6%	-27.5‰ -27.5‰
IOE Big Lake 13-25	77.0% 76.6%	-27.1‰ -27.1‰
GOC Zama 12-21	63.5% 73.1%	-27.9‰ -28.0‰
IOE Virgo 5-11	73.1% 77.4%	-28.4‰ -28.4‰
IOE Leduc 8-9	75.2% 74.0%	-28.5‰ -28.4‰
GOC Erskine 6-19	69.0% 70.8%	-27.3‰ -27.9‰
GOC Stettler 16-9	73.9% 75.9%	-27.8‰ -27.5‰
GOC Stettler 12-3	72.4% 72.6%	-27.5‰ -27.1‰

Carbon Percent Pooled SD = 2%

δC^{13}_{PDB} Pooled SD = 0.2‰

TABLE I-IV

REPLICATE CARBON YIELDS FOR $Cd(CH_3COO)_2$

94.0
92.5
92.4
90.5
93.0
90.0
88.00
92.0
93.0
92.0
93.0
94.1
95.1
92.8
90.4
91.4

N = 16

Mean = 92.1%

Standard Deviation = 1.8%

TABLE I-V

MEAN δC^{13}_{PDB} VALUES FOR THE IMPERIAL OIL LABORATORY STANDARDS

Standard No.	Mean δC^{13}_{PDB} Value	Standard Deviation	N	Imperial Oil δC^{13}_{PDB} Value
57898	-30.7‰	0.19‰	9	-30.4‰
58396	-28.9‰	0.26‰	6	-28.3‰
58461	-28.9‰	0.25‰	9	-28.7‰
58509	-26.8‰	0.18‰	12	-26.6‰

The isotope reproducibility and accuracy of the wet oxidation procedure was determined by doing replicate extractions and isotope ratio measurements on four oils obtained from the Imperial Oil Company in Calgary. The carbon isotope ratio of these oils had been determined several times on carbon dioxides derived using the copper oxide furnace combustion method. Table I-V lists the means of replicate carbon isotope analyses of these oil standards together with the mean δC^{13} values determined by Imperial Oil Research in Calgary. Except for oil 58396, the carbon isotope analyses of these oil standards, processed using the wet oxidation procedure, agree with the Imperial Oil data within the determined reproducibility of 0.2‰. This reproducibility was calculated by pooling the standard deviations determined for the means of each of the four oil standards. It agrees with the standard deviation determined by pooling the estimated standard deviations of the duplicate oil analyses. Oil 58396 was the most volatile oil of the four standards and loss of the light ends to atmosphere before closure of the oxidation system was probably responsible for the discrepancy in the δC^{13} values. Generally, carbon dioxide derived using the wet oxidation procedure contains slightly more C^{12} than carbon dioxide generated using the copper oxide furnace combustion technique.

c) Carius Tube-Cupric Oxide Oxidation Method

The Carius tube oxidation method oxidized refined oils and the saturate and aromatic fractions of oils using powdered cupric oxide at

600°C. The reaction vessel used in this method consisted of a breakseal made from 12 mm O.D. pyrex with two side arms blown on (see Figure I-11). About 150 mg of purified copper (II) oxide was poured to the base of the reaction vessel, through the lower side arm, using a specially made small funnel. The uppermost portion of the lower side arm was then drawn off and this breakseal was attached to the extraction line using a teflon ultra torr union. Both the breakseal and cupric oxide were then outgassed to high vacuum and the breakseal was checked for leaks to atmosphere. Three to six Carius tubes-breakseals could be processed simultaneously through this stage. After the outgassing step was completed, the breakseals were removed from the vacuum line and loaded with about 3 mg of oil. To do this, the lower side arm was opened and a narrow eye dropper containing the oil sample was lowered to a point just above the black copper oxide reagent. One approximately 3 mg drop of oil was allowed to fall directly onto the cupric oxide. The lower side arm was then drawn off quite close to the sides of the Carius tube (see Figure I-12). The Carius tube was then attached to the vacuum line and the oil sample frozen to liquid nitrogen temperatures. After a freezing period of 2 minutes, the vapour pressure of the oil was reduced sufficiently to begin the evacuation of the Carius tube to high vacuum. Again, three to six breakseal-Carius tubes could be processed through this stage. After being pumped to high vacuum, each Carius tube was removed from the vacuum line by drawing off the upper side arm at its thickened portion (see Figure I-11). The Carius tubes were then removed from

FIGURE I - 11

CARIUS TUBE REACTION VESSEL

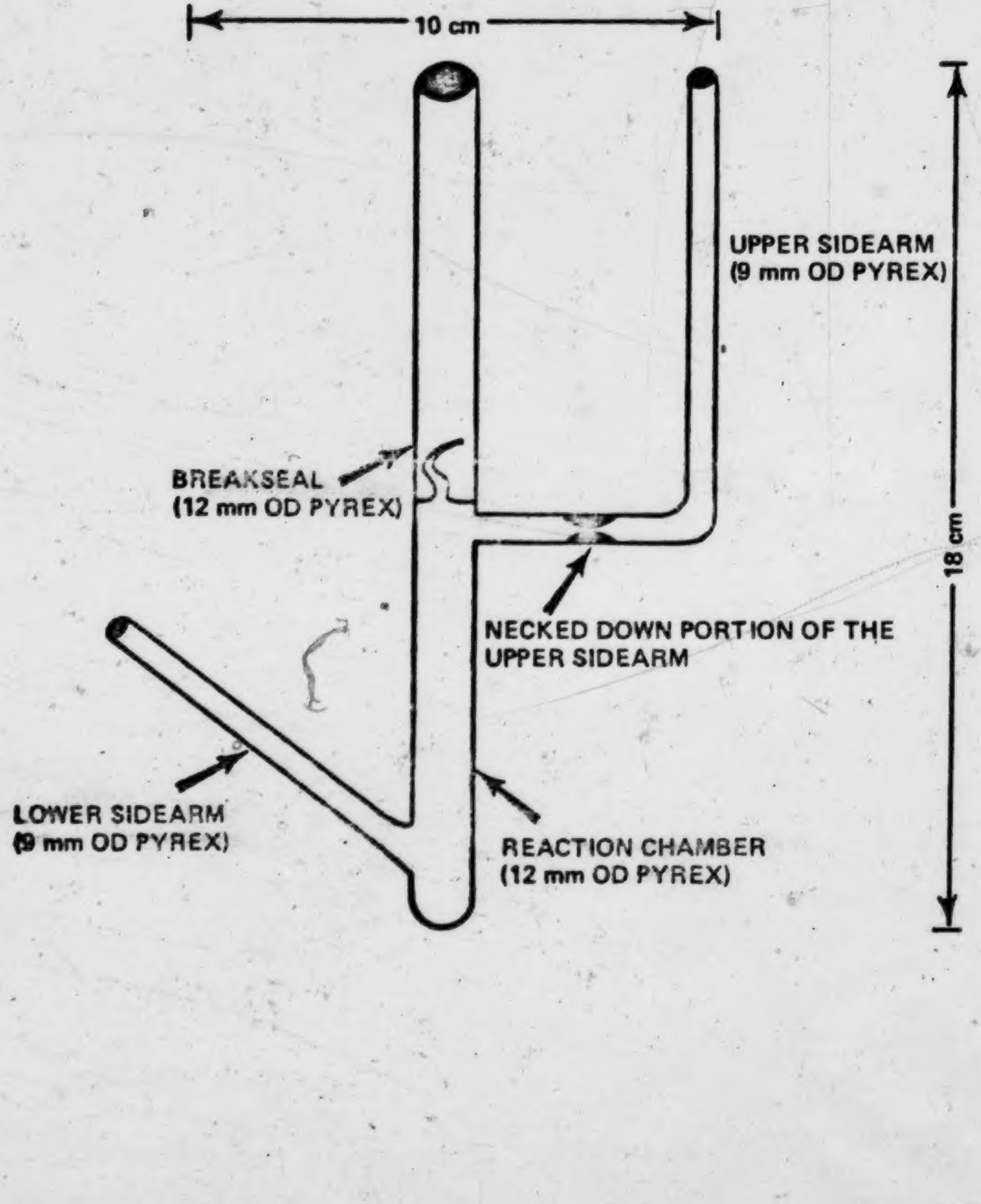
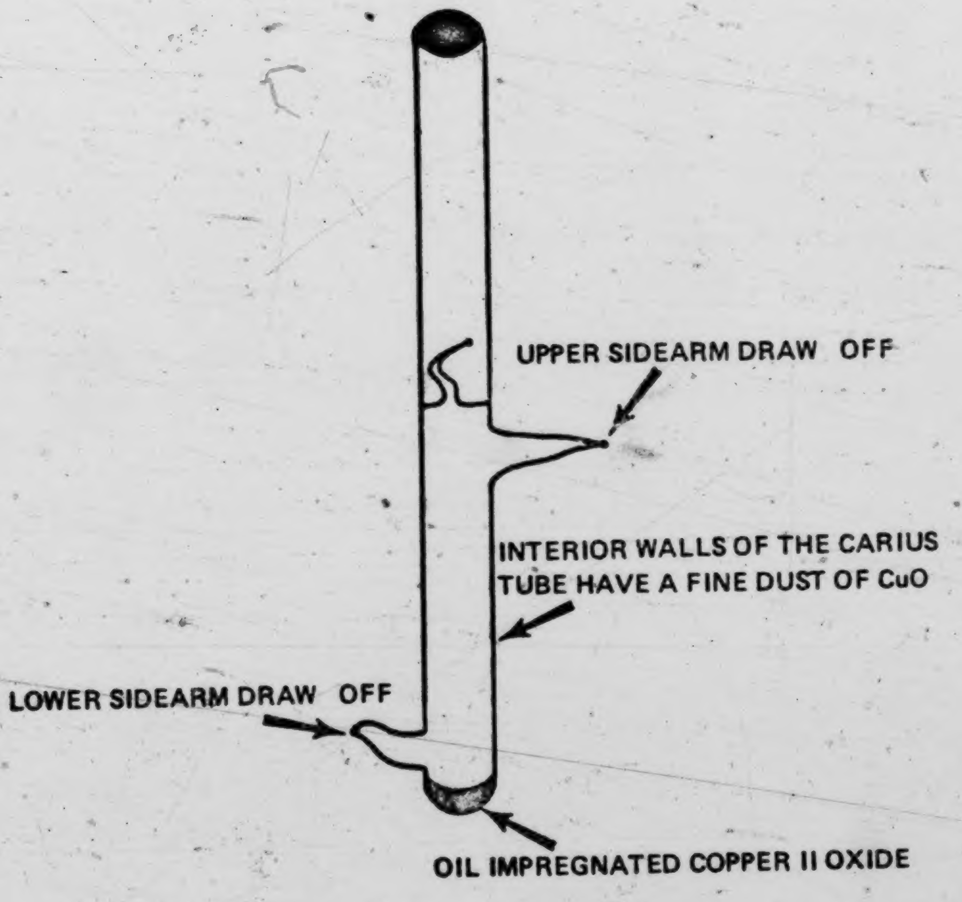

10 cm
UPPER SIDEARM
(9 mm OD PYREX)
BREAKSEAL
(12 mm OD PYREX)
18 cm
NECKED DOWN PORTION OF THE
UPPER SIDEARM
LOWER SIDEARM
(9 mm OD PYREX)
REACTION CHAMBER
(12 mm OD PYREX)

FIGURE I - 12

EVACUATED TUBE CONTAINING CuO AND THE OIL SAMPLE

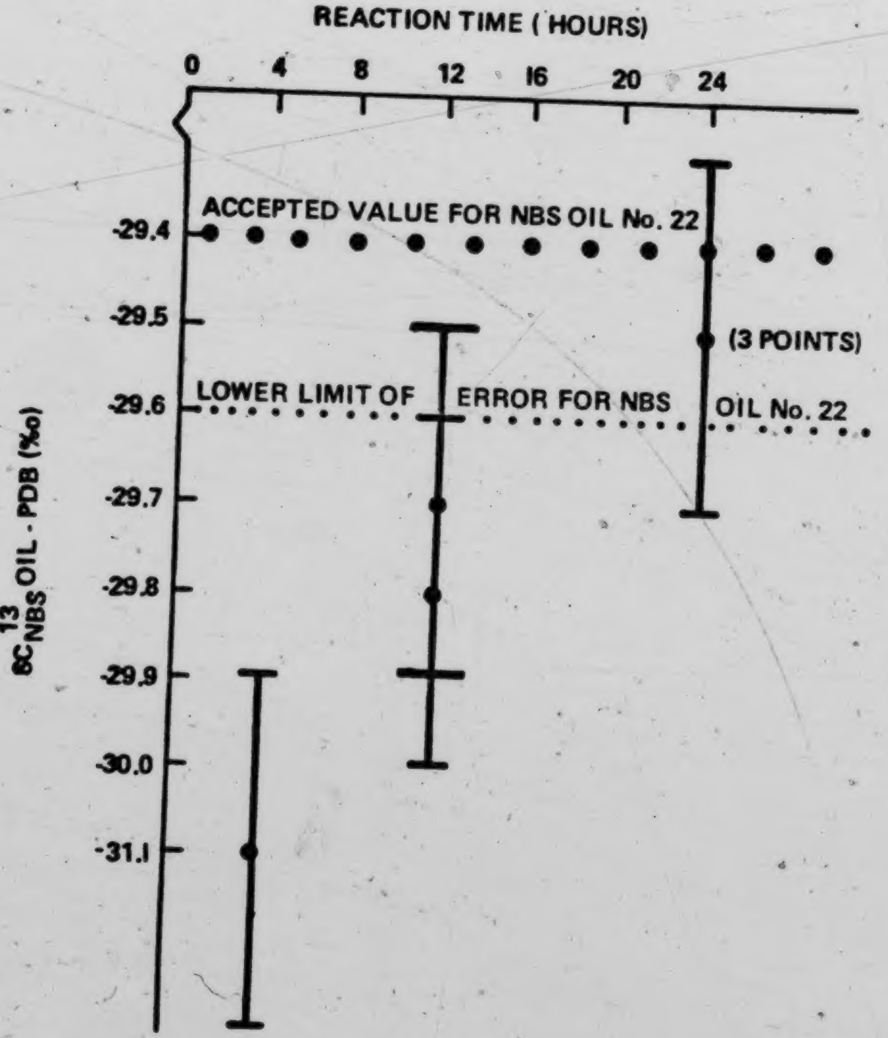

UPPER SIDEARM DRAW OFF
INTERIOR WALLS OF THE CARIUS TUBE HAVE A FINE DUST OF CuO
LOWER SIDEARM DRAW OFF
OIL IMPREGNATED COPPER II OXIDE

their liquid nitrogen dewars and allowed to come to room temperature. Any loose cupric oxide was distributed evenly through the breakseal. Six Carius tubes were then placed on a specially made asbestos stand in a muffle furnace and arranged so that there was minimal touching of their parts. The furnace was then heated to 600°C and the reaction let run for a period of 24 hours. Shorter reaction times tended to produce more C^{12} - enriched carbon dioxide (see Figure I-13). After the 24 hour oxidation period was over, the Carius tubes were removed from the furnace while the pyrex was still soft and placed to cool on an asbestos mat. Since the reaction temperature was about 20°C hotter than the yielding point of pyrex, the reaction vessels were expanded outwards by the pressure of the oxidation products. The oil sample size (3 mg) and the internal volume of the Carius tube (12 std. cc) were chosen so that the pressure of the reactants and products would not greatly exceed one atmosphere at 600°C. Therefore, as long as the reaction vessels were not overloaded they remained intact and none of the oxidation products leaked to atmosphere. In the case where a small oil sample was run, the sides of the Carius tube collapsed together There was, however, still enough free space to allow the removal of the reaction products.

The oxidation products, carbon dioxide and water, were extracted from the carius tubes, separated and purified, using the same apparatus and procedure as was used for the wet oxidation method. One further step was necessary; that was the water frozen down in

FIGURE I - 13

PLOT OF REACTION TIME VS δC^{13}_{PDB} FOR NBS OIL No. 22



NOTE: THE ERROR BARS DELINEATE A 2σ INTERVAL WHOSE VALUE IS 0.4‰

the acetone-dry ice cold trap had to be transferred to a breakseal to be stored for hydrogen-deuterium analysis.

For carbon dioxides produced by the Carius tube method, error in δC^{13} analyses due to the production of carbon monoxide and contamination by atmospheric carbon dioxide had to be assessed.

Thermodynamic calculations (see Appendix II) show that the equilibrium partial pressure of carbon monoxide in the reaction vessel at 600°C was negligible, approximately 7×10^{-30} atm. The fractionation factor for the reaction:

$$C^{13}O + C^{12}O_2 \rightleftharpoons C^{12}O + C^{13}O_2$$

is 1.018 at 600°C (Urey, 1946; Bottinga, 1968; Schwartz et al. 1969). Assuming that the average Devonian oil δC^{13}_{PDB} value is approximately -28‰ (Degens, 1969) and using the method described by Ohmoto (1972), the calculations presented in Appendix II show that the disparity between the δC^{13} values of CO and CO_2 is not great enough for the mole fraction of carbon monoxide produced to cause the δC^{13} value of the carbon dioxide to be significantly different from the δC^{13} value of the total carbon oxidized, that is, the δC^{13} value of oil.

Calculations in Appendix III show that the small amount of isotopically heavy atmospheric carbon dioxide that was frozen down with the oil sample did not appreciably affect the del value of the carbon dioxide produced from the combustion of the oil. The contaminant CO_2 was frozen out from a 25 cc volume which included the Carius tube reaction vessel and a portion of the vacuum line. In the calculations, it was assumed that the air occupying this volume contained 0.03 vol.% CO_2 and that the del value of the CO_2 was -7.1 per mil PDB. The smallest oil sample oxidized, 4.46×10^{-5} moles of carbon dioxide whose del value was -28‰ PDB, would be contaminated by 3.09×10^{-7} moles of atmospheric CO_2. The del value of of the carbon dioxide mix was calculated to be -27.9 per mil. Considering an analytical error of ±0.2‰, then this del value is not significantly different from the del value of the carbon dioxide produced solely from the oxidation of the oil sample. If very small samples are to be oxidized using the Carius tube method, care should be taken to reduce atmospheric contamination. The effect of atmospheric water on the hydrogen-deuterium ratio of the oil sample was not calculated. However, it will depend on the absolute humidity and the effect could be substantial.

The carbon isotope accuracy and reproducibility for the Carius tube oxidation method was determined by analyzing ten preparations of NBS Oil Standard #22 (see Table I-VI). The mean carbon isotope del value was -29.6‰ and the standard deviation of the ten analyses

TABLE I-VI

CARBON ISOTOPE ANALYSES OF NBS OIL NO. 22

Run Number	δC^{13}_{PDB}
A9-4	-29.6‰
A10-1	-29.7‰
S4-5	-29.3‰
S5-1	-29.8‰
S10-6	-29.8‰
C1	-29.4‰
C2	-29.5‰
C3	-29.5‰
C11	-29.9‰

Mean δC^{13}_{PDB} = -29.6‰

SD = ±0.2‰

Accepted δC^{13}_{PDB} = -29.4‰

was 0.2‰. In view of the analytical errors, agreement with the accepted del value for NBS Oil, which is -29.4‰, is good. However, it appears that, like the wet oxidation method, the Carius tube technique produces slightly C^{12} - enriched carbon dioxide.

It is necessary to point out that the Carius tube method was used in this work to oxidize only the saturate and aromatic fractions of oils. The more complex NSO and asphaltene compounds were separated out using liquid chromatography (see this chapter, Section 6). NBS Standard #22 is a refined lubricating oil which also contains no NSO or asphaltene fractions. Consequently, the ability of the Carius tube method to oxidize whole oils to give a carbon dioxide, whose del value is reproducible and accurate by comparison to the copper oxide combustion furnace method, is untried.

Section 5: Separation and Combustion of Natural Gas Components

a) Introduction

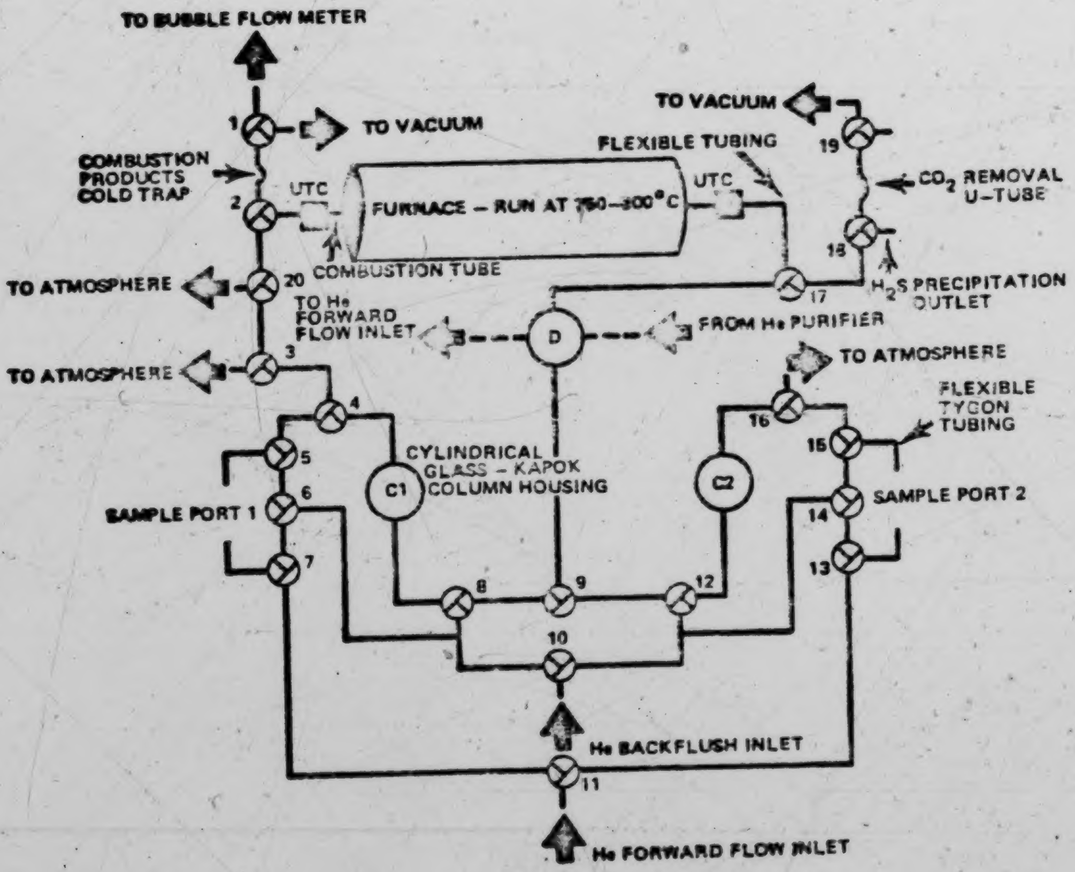
A sample consisting of 4 standard cc of natural gas was chromatographed using a 6-foot glass column packed with porapak-Q. The individual hydrocarbon peaks up to and including C_3 were directed to a flow path through a copper oxide furnace at 800°C (see Figure I-14). Each hydrocarbon component was burned in sequence and the combustion products transferred in their turn to a vacuum line. Here, carbon dioxide and water were separated, purified and transferred to glass breakseals for isotope analysis. The non-hydrocarbon gases N_2, CO_2, H_2S, and H_2O were diverted past the furnace tube to a sample outlet. Nitrogen, carbon dioxide and water were exhausted to the atmosphere. Hydrogen sulphide was recovered as a cadmium sulphide precipitate, converted to silver sulphide and then burned to sulphur dioxide for sulphur isotope analysis. Sample size, helium carrier gas flow rate and combustion tube length and temperature were chosen to assure total combustion of the hydrocarbon gases to water and carbon dioxide. The helium carrier gas flow rate and gas sample size were also chosen so that there was adequate separation between gas peaks to allow the transfer of each hydrocarbon's combustion products to the vacuum portion of the flow line without overlap with the combustion products from other hydrocarbon gases or interference from the non-hydrocarbon peaks.

b) Gas Chromatograph Design

The natural gases to be analysed contained both hydrocarbon and non-hydrocarbon components. As a result it was necessary to choose a column-active solid and detector that would resolve and detect N_2, O_2, CO_2, H_2S, H_2O, and the hydrocarbon gases up to and including C_3H_8. To further complicate the chromatograph design, hydrogen sulphide was present in the natural gas samples in concentrations up to 55 volume percent. Therefore, a corrosion resistant detector and flow line was required. Although H_2S remains inert to a stainless steel or copper flow line in the absence of water, it was found to be virtually impossible to maintain anhydrous conditions. Consequently, an all glass chromatograph system was designed (see Figure I-14). The only portion of this system that was metal, and was exposed to H_2S, was the detector unit. Its volume, however was comparatively small and loss of hydrogen sulphide by reaction with the stainless steel detector housing would produce negligible error in the analysis for the size of the gas sample run. Since both hydrocarbon and non-hydrocarbon gases were being analysed, it was necessary to use a thermal conductivity detector. The detector filaments were made of nickel and were therefore reasonably resistant to hydrogen sulphide. Porapak-Q was chosen as the packing for the glass columns. This active solid does not resolve nitrogen from oxygen and it was therefore not possible to routinely check for air contamination in the samples. On the other hand, the resolution of the combined N_2-O_2 peak and the CH_4, CO_2, C_2H_6, was

FIGURE I - 14

NATURAL GAS COMPONENT SEPARATION AND COMBUSTION APPARATUS


TO BUBBLE FLOW METER
1
TO VACUUM
COMBUSTION PRODUCTS COLD TRAP
2
UTC
FURNACE – RUN AT 750–800°C
UTC
FLEXIBLE TUBING
TO VACUUM
19
CO2 REMOVAL U-TUBE
18
COMBUSTION TUBE
TO ATMOSPHERE
20
17
H2S PRECIPITATION OUTLET
TO He FORWARD FLOW INLET
D
FROM He PURIFIER
TO ATMOSPHERE
3
TO ATMOSPHERE
4
16
FLEXIBLE TYGON TUBING
5
CYLINDRICAL GLASS – KAPOK COLUMN HOUSING
15
C1
C2
SAMPLE PORT 1
6
SAMPLE PORT 2
14
7
13
8
9
12
10
He BACKFLUSH INLET
11
He FORWARD FLOW INLET

LEGEND

UTC: ULTRA TORR CONNECTOR (¼")

D : THERMAL CONDUCTIVITY DETECTOR

C : 6' POROPAC Q COLUMN –
STANDARD WALL 8 MM OD PYREX

⊗ : 2 MM 2-WAY GROUND GLASS STOPCOCK

FLOW LINE MADE OF 8 MM OD PYREX

excellent. Helium was used as a carrier gas because of its inertness, high degree of purity (99.99%), much greater thermal conductivity than the hydrocarbon and non-hydrocarbon gases, and its absence or extremely low abundance in the sample gases to be analysed. The carrier gas was purified further by passing it through an on-line composite trap in which carbon dioxide and water were removed. This trap consisted of a 30 x 3.5 cm glass tube packed with 15 cm of 20-30 mesh ascarite, at the up flow end, and 15 cm of MCB anhydrone, at the downflow end.

Despite the high degree of purity of the helium carrier gas, an impurity of less than 1/10,000 caused significant contamination when a liquid nitrogen cold trap was placed in the flow system. To define the nature of the contaminant, a dewar of liquid nitrogen was applied to the combustion products U-tube (see Figure I-14) and purified helium was passed through the system for a period of 5 minutes. The contaminant was then transferred to the vacuum line where its vapour pressure and colour were recorded. Its clear colour and vapour pressure of 18 mm Hg at 22°C suggested that it was water. No significant quantity of carbon dioxide was found in the contaminant. The quantity of this contaminant that would be frozen down with the combustion products, from the burns of the individual hydrocarbons, would depend on the length of the freezing period. This period of time was, on the average, 1.6 ±0.1 min., 3.9 ±0.4 min. and 14.8 ±2.1 min. for methane, ethane and propane, respectively. If this contaminant were water, its effect on the hydrogen isotopes of the hydrocarbon gases would depend on the magnitude of the value Δw and on X_{wc}, where Δw is defined as:

$$\Delta^{w} = {}^{D}\text{Hydrocarbon water} - {}^{D}\text{Contaminant water}$$

and X_{wc} is defined as:

$$X_{wc} = \frac{\text{moles contaminant water}}{\text{moles contaminant water + moles water of combustion}}$$

The larger the Δw and X_{wc} factors, the more serious would be the effect of the contaminant on the H/D ratio of the hydrocarbons. In a natural gas, the order of components methane, ethane and propoane is that of decreasing relative abundance and increasing length of time over which their products of combustion were frozen down. As a result, the H/D ratio of methane should be least affected by the contaminant as compared to ethane or propane. The impurity in the helium carrier gas did not affect the C^{12}/C^{13} ratios of the hydrocarbon gases.

Experiments were completed to define the gas sample size, the chromatograph column length and temperature, carrier gas flow rate, and the thermal conductivity cell conditions which would result in the adequate separation and quantitative detection of the natural gas components in as short a time as possible. Relatively large gas samples had to be run in order to collect enough combustion products for isotope analysis from only one or two runs of a sample gas. Since each hydrocarbon peak was being combusted on line, it was necessary to separate the gas components enough to allow the complete combustion of a hydrocarbon peak, the collection of its combustion products and the transfer of these to the vacuum line without any interference from the other gas components. The conditions which met these requirements are listed in Table I-VII. A typical chromatogram of a 4 standard cc natural gas sample is illustrated in Figure I-15. Average retention times for the gas components are listed in Table I-VIII. In Table I-VIII, the observed trend of an increasing standard deviation for the retention times, with increasing length of retention time, is a result, in part, of imprecise controls on column temperature and carrier gas flow rate. The columns were brought to 35°C just prior to each run, by filling their glass-kapok insulating housings with an appropriate mixture of hot and cold water (see Figure I-14). The gas flow rate was set just before sample injection at around 60 ml per minute. As the run progressed, column temperature decreased and flow rate therefore increased. Retention properties of the column would adjust accordingly (Beckman Chromatograph Manual). At the end of the run, the column temperature was generally at 25°C to 30°C and flow rates were at 50 to 60 ml per minute. Another factor affecting the retention time standard deviation was the abundance of a component. It was found that as component abundance increased, its retention time decreased. This last factor probably had the

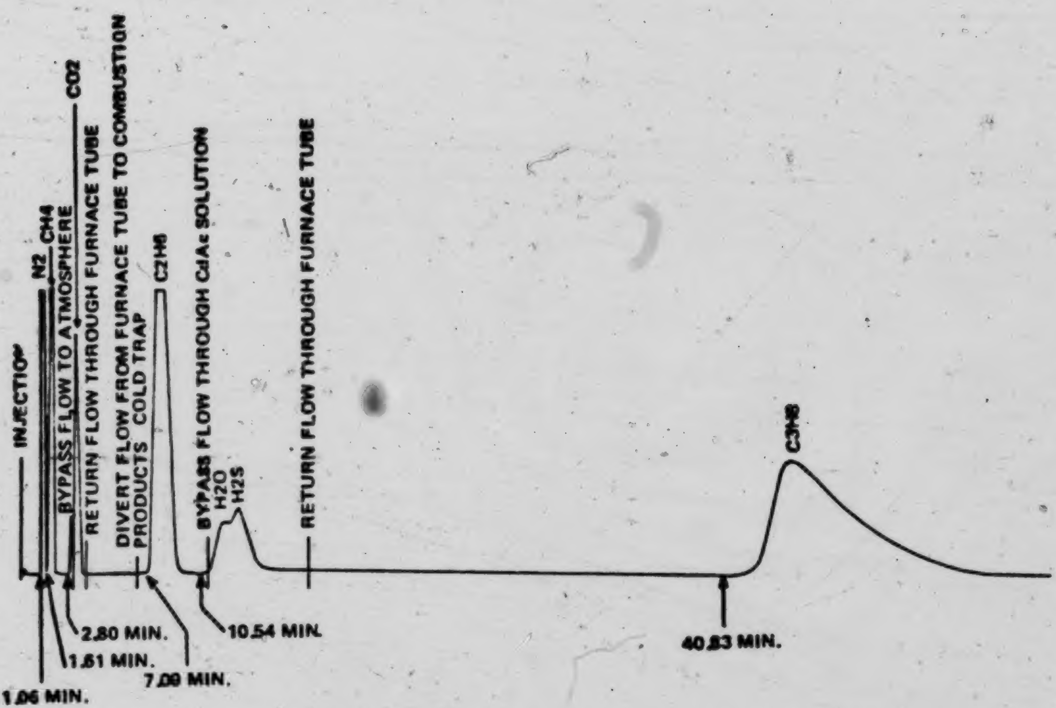
TABLE I-VII

CHROMATOGRAPH SPECIFICATIONS

Flow Line:	Type - 8 mm OD standard wall pyrex Valve Type - Two way low vacuum ground glass stopcocks. Apiezon N vacuum grease was used as a seal-lubricant.
Carrier Gas:	Type - Helium Purity - 99.99% Flow Rate - 55 to 60 ml per minute
Column:	Type - 8 mm OD standard wall pyrex Length - 6 feet Packing - Porapak type Q, 50-80 mesh Temperature - 30°C to 35°C
Detector:	Type - Thermal conductivity cell Temperature - Room (22°C to 23°C) Bridge current - 150 mA Specifications - 4 filament Gow-Mac type W-1 with nickel detector elements
Recorder Type:	Hewlett-Packard model 7101B
Combustion Tube:	Type - 9 mm OD standard wall Silica glass Length - 48.5 cm Temperature - 780°C to 800°C Oxidant type - CuO 99.95% pure Oxidant charge - 19 cm central length of the furnace tube 3/4 filled with black copper oxide Oxidant Average $\delta O^{18}_{PDB} = -20.2$‰
Gas Sample Size:	4 standard cc

FIGURE I - 15

NATURAL GAS CHROMATOGRAM



NATURAL GAS No. GOC NEW NORWAY 11-36-44 -22 W4
FLOW RATE : 55-60 ML/MIN
HE CARRIER GAS; 6' PORAPAC Q COLUMN AT 35° C
THERMAL CONDUCTIVITY DETECTOR AT RM. TEMP. 22° C
BRIDGE CURRENT AT 150 MA
4 STANDARD CC GAS SAMPLE
CHART SPEED = ½ INCH/MIN.

TABLE I-VIII

SELECTED RETENTION TIMES

[Retention Times are quoted in minutes.]

Sample Description	N_2	CH_4	CO_2	C_2H_6	H_2O	H_2S	C_3H_8
IOE Yekau Lake 8-4-52-26 W4M	1.32	1.89	3.62	9.29	14.49	-	52.08
GOC Zama 12-21-117-4 W6M	1.18	1.65	2.95	8.28	12.12	12.99	50.46
GOC Zama 4-36-116-6 W6M	1.26	1.57	2.69	7.98	-	12.76	47.30
Amoco Beaver River #B-1	1.24	1.61	3.07	8.83	12.48	13.23	-
GOC Virgo 5-27-114-5 W6M	1.25	1.62	3.09	7.87	-	12.28	45.32
Aquitaine Ricinus 7-13-36-10 W5M	1.25	1.65	3.08	8.35	-	11.29	ND
GOC Zama 7-7-116-5 W6M	1.19	1.62	2.98	7.63	-	12.29	45.94
IOE Acheson 4-10	1.25	1.94	3.75	10.24	15.83	-	61.88
Golden Spike 10-27	1.18	1.79	3.57	9.76	15.12		58.96
IOE Big Lake 9-23-53-26 W4M	1.25	1.76	3.23	7.95	12.32	12.99	45.42
GOC So. Calmar 5-2-49-27 W4M	1.26	1.72	3.29	8.18	12.59	-	49.56
GOC Westerose Carl 12	1.14	1.46	3.09	7.73	11.64	12.36	43.20
GOC Swanson Stettler 16-16-38-20 W4M	1.10	1.50	3.00	8.38	-	13.54	51.20
GOC West Drumheller 12-7-30-21 W4M	1.23	1.62	3.01	8.03	-	12.92	46.18
Sunoco Malmo 5-14-44-22 W4M	1.22	1.57	3.14	8.03	-	12.83	48.84
GOC Erskine 8-13-39-21 W4M	1.26	1.72	3.15	8.03	-	12.30	48.22
Aquitain Strachan 7-32	1.30	1.80	3.53	9.53	-	14.49	61.16
GOC New Norway 11-36-44-22 W4M	1.25	1.82	3.22	7.94	11.95	12.76	43.60
HBOG Sylvan Lake Cond. gas	1.22	1.58	3.38	9.37	-	14.49	59.60
Tex. Can. Ltd. Bonnie Glen #CRB-10	1.14	1.65	3.31	8.66	13.31	-	56.40
Av. retention times (mins)	1.22	1.68	3.21	8.50	13.19	12.90	50.85
Standard Deviation (1σ)	0.04	0.13	0.20	0.75	1.32	0.39	6.16

N = 20

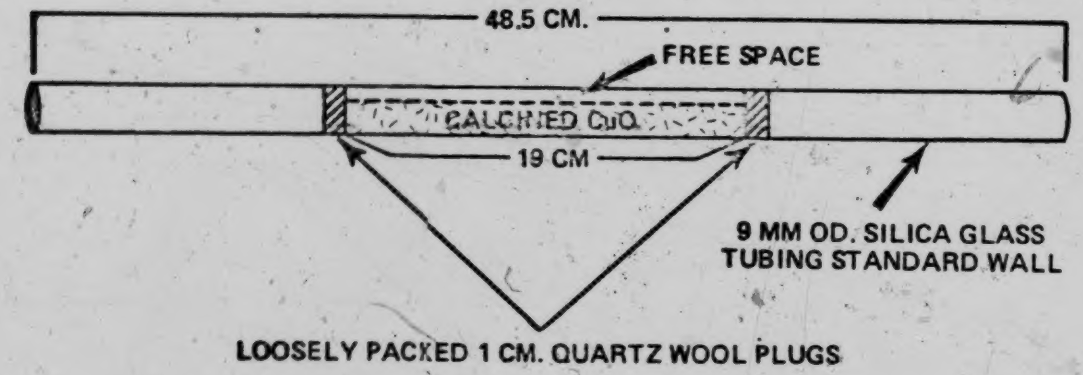
greater effect on the standard deviation since increasing flow rate and decreasing column temperature can be opposing factors.

c) Gas Component Combustion System Design

A combustion system was designed so that, on one pass through the furnace, a 4 standard cc natural gas sample (that was entrained in a helium carrier gas flowing at a rate of 50 to 60 ml per minute) would be combusted to water and carbon dioxide with near 100% efficiency. Although testing was not exhaustive, the combustion tube design and oxidant configuration found to be effective is shown in Figure I-16. The free space over the copper (II) oxide reagent allowed nearly unimpeded gas flow. The roughness of the oxidant's surface and convection within the furnace tube resulted in sufficient turbulent mixing to combust no less than 99.98% of the methane component of a natural gas laboratory standard and 100% of the less abundant ethane and propane homologs. Chromatograms of this natural gas standard run before and after combustion are shown in Figures I-17 and I-18. Fisher reagent grade black copper oxide powder (CuO) with a purity of 99.95% was used as the oxidizing agent. Its performance at combustion temperatures of 790°C to 800°C was found to be better than red copper oxide (Cu_2O) powder. The copper (II) oxide reagent was calcined at 500°C in a pyrex tube that was continuously evacuated to pressures of less than 10^{-4} torr for a period of 48 hours. This procedure ensured that no impurity that could oxidize to carbon dioxide and water remained in the

FIGURE I - 16

OXIDATION TUBE DESCRIPTION


48.5 CM.
FREE SPACE
CALCINED CuO
19 CM
9 MM OD. SILICA GLASS TUBING STANDARD WALL
LOOSELY PACKED 1 CM. QUARTZ WOOL PLUGS

NOTE: THE CuO OXIDANT OCCUPIES ½ TO ¾ OF THE SPACE BETWEEN THE QUARTZ WOOL PLUGS

FIGURE I - 17

NATURAL GAS CHROMATOGRAM – PRE COMBUSTION

CHROMATOGRAM: REDWATER SALES GAS
FLOW RATE: 55 – 60 ML/MIN
HE CARRIER GAS; 6' PORAPAC Q COLUMN AT 35° C
T.C. DETECTOR AT 22° C (NI FILAMENTS)
150 MA. BRIDGE CURRENT
4 STD. CC GAS SAMPLE
CHART SPEED: ½ INCH/MIN

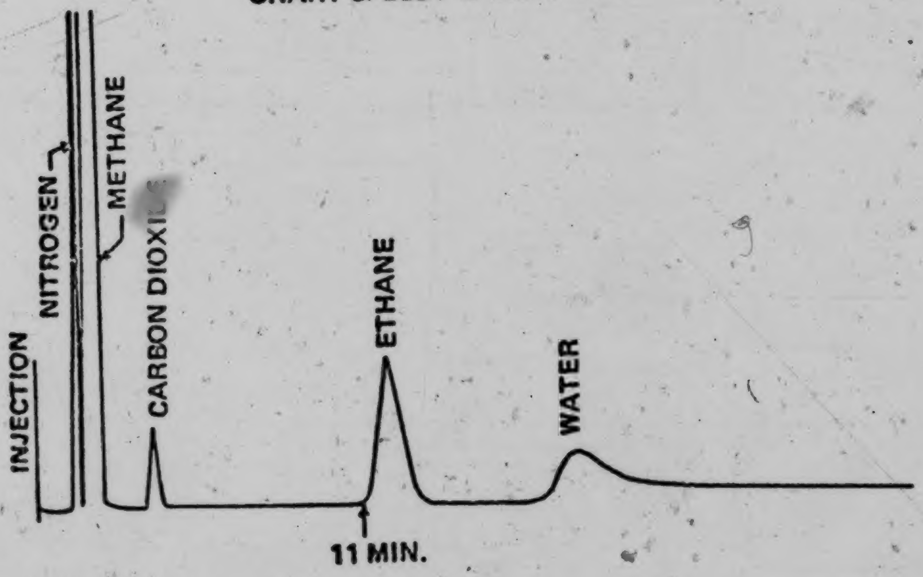
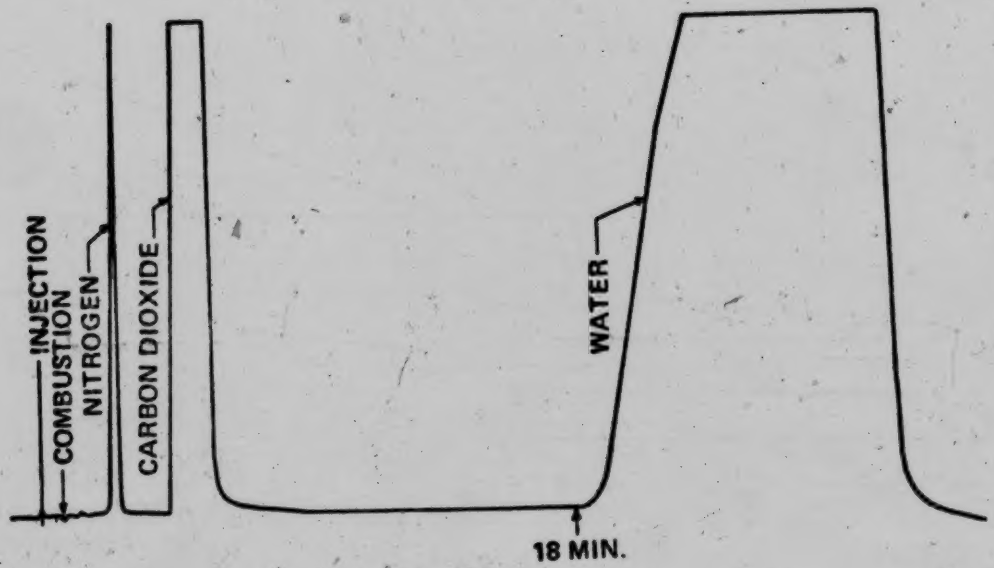


FIGURE I - 18

CHROMATOGRAM OF COMBUSTED REDWATER SALES GAS



CHROMATOGRAM: COMBUSTED REDWATER SALES GAS
HELIUM CARRIER GAS AT 55 – 60 ML/MIN.
6' PORAPAK Q COLUMN AT 35° C
T.C. DETECTOR AT 22° C (NI FILAMENTS)
150 MA. BRIDGE CURRENT
4 STD CC GAS SAMPLE
¼ INCH/MIN CHART SPEED

oxidizing agent.

Also, prior to the first combustion of each day, the CuO combustion tube charge was heated to reaction temperature in the helium flow for a period of one hour. Blank runs confirmed that the purified copper oxide reagent added no water or carbon dioxide contaminant to the combustion system. A combustion temperature of 800°C was used since it was in a range recommended for efficient hydrocarbon combustion (Calvin _et_ _al_. 1949).

Experiments were completed to determine the oxidation efficiency of the copper (II) oxide reagent. After ten burns of 4 standard cc natural gas samples, the efficiency of the oxidizing reagent remained at a level greater than 99.98% (refer to Table I-IX). The oxidant was examined and found to be expended, by reduction to cuprous oxide and other copper sub-oxides, only along a 3 to 5 cm length at the up-flow end of the combustion tube. Consequently the combustion tube was turned around and used for another ten runs with an equally high level of oxidation efficiency. After this, a new combustion tube was used. The old one was cleaned and recharged. The number of oxidations required to reduce the efficiency of the combustion tube to a level that would produce a significant error in the carbon and hydrogen isotope analyses was not determined. However, an oxidation efficiency of 99.98% for methane produced no carbon isotope error. In the tests run to determine the oxidation efficiency of the copper oxide furnace, complete

TABLE I-IX

OXIDATION EFFICIENCY OF THE CUO FURNACE

Combustion Order	Sample Gas Volume	Methane Peak Area (in^2)	Uncombusted Methane Peak Area (in^2)	Fraction Methane Uncombusted
1	4 std. cc.	40 $in.^2$	not determined	
2	4 std. cc.	40 $in.^2$	not determined	
3	4 std. cc.	40 $in.^2$	not determined	
4	4 std. cc.	40 $in.^2$	not determined	
5	4 std. cc.	40 $in.^2$	not determined	
6	4 std. cc.	40 $in.^2$	none detected	0.00
7	4 std. cc.	40 $in.^2$	none detected	0.00
8	4 std. cc.	40 $in.^2$	<0.01 $in.^2$	<1/4,000
9	4 std. cc.	40 $in.^2$	<0.01 $in.^2$	<1/4,000
10	4 std. cc.	40 $in.^2$	<0.01 $in.^2$	<1/4,000

natural gas samples were combusted and the effluents from the furnace tube chromatographed. Of the ten tests done on the final furnace design, the worst yields observed for the oxidation of the methane component were better than 99.98%. No uncombusted C_2H_6 or C_3H_8 could be detected (refer to Figure I-18). During the routine combustion of the natural gas samples, only the chromatographed hydrocarbons were oxidized. The performance of the combustion tube should therefore be equal to, if not better than, its test performance due to the smaller volume of hydrocarbon being oxidized.

d) Chromatograph Design Restrictions

The assembled chromatograph system is illustrated in Figure I-14. The ground glass two-way stopcocks were found to be the main weak link in the flow line design. These stopcocks were greased with Apiezon type N compound and when flow pressures of 15 to 20 psig were reached at a room temperature of 22°C, the stopcocks leaked to atmosphere. When room temperature climbed to 27°C, which fortunately was seldom, the apiezon grease had a vastly reduced viscosity and the stopcocks would not function at pressures greater than 2 to 3 psig. The other weak point in the chromatograph design was the connection of the quartz glass furnace tube to the pyrex flow line. This seal was made with 1/4-inch ultra torr unions. As long as the glass surfaces at the joins were clean, not damaged and of the proper diameter (9 mm), the seal did not leak at the flow pressures used.

Helium carrier gas flow rates of 55 to 60 ml per minute were achieved at a tank outlet pressure of 5 to 10 psig as a result of the column length, type of packing, column temperature, and the furnace tube design. This pressure is well within the strain limits of the glass line and stopcock design. The low flow pressures permitted the joining of the metal thermal conductivity cell ports to the glass flow line with wire clamped tygon tubing. The alternate join would have been a more expensive, less strain resistant kovar seal. Tight connections between the flow line and the sample injection U-tubes could also be made with tygon tubing as a result of the low flow pressures.

e) Gas Sample Injection

Gas from a glass storage container was transferred to an injection U-tube using the vacuum expansion technique outlined in Appendix IV. The contained gas sample was then injected into the chromatograph system by diverting the flow path through the U-tube according to the procedure given in Appendix V. Air contamination of the sample using the outlined transfer and injection procedures should be minimal. However, if the nitrogen, carbon dioxide and water contents of the gas sample were required in the analysis, the precise extent of the air contamination would have to be determined.

f) Gas Component Combustion

The following procedure was developed to recover the products from the combustion of the hydrocarbon components of a natural gas. Just prior to the appearance of a hydrocarbon peak on the recorder, a dewar of liquid nitrogen was applied to the combustion products U-tube (see Figure I-14). As the hydrocarbon component was oxidized in the furnace to carbon dioxide and water, the helium carrier gas flushed these combustion products through to the U-tube where they were frozen out. The carrier gas passed through the U-tube and was exhausted to atmosphere through two-way stopcock 1 (see Figure I-14). However, part of the water precondensed onto the sides of the glass line down flow from the furnace tube. This water was transferred to the combustion products cold trap by lightly flaming the sides of the line with an oxy methane torch. Once all of the combustion products had been transferred to the U-tube, high vacuum two-way stopcock 2 was turned, isolating the cold trap from the flow line and diverting the gas flow from the furnace tube through stopcock 20 to atmosphere. Two-way stopcock 1 was then turned to the CB flow position, isolating the U-tube from the atmosphere. In the combustion of methane, the transfer of water and carbon dioxide to the U-tube cold trap had to be rapid in order to avoid any contamination from the closely following carbon dioxide gas peak. On the average, this transfer had to be completed in less than 1-1/3 minutes. By flaming the glass flow line, this was entirely possible. The methane component - carbon dioxide peak separation in the column was therefore critical. Because of the rapidity of the methane combustion products transfer, the transfer was probably not complete. However, no measurable error was incurred in the carbon isotope analysis as a result of this (see Table I-X). Ample time was available for near 100% transfer of carbon dioxide and water from the combustion of ethane and propane.

g) Isolation and Purification of the Combustion Products

Water and carbon dioxide were transferred from the cold trap in the chromatograph flow line to the vacuum line where they were isolated and purified using the vacuum transfer and distillation procedures outlined in Appendix VI. Since the vacuum line was designed to have storage capacity, the volume of combustion products could be augmented from multiple burns of the same gas. Therefore, a paraffin homolog of low abundance could be analyzed isotopically. As a rule, one standard cc of carbon dioxide (44.6 micromoles) was the smallest sample that could be run reproducibly on the mass spectrometer. In practice, a 4 standard cc volume of natural gas always gave at least one standard cc of carbon dioxide from the combustion of the methane component. Usually, the combustion of ethane also gave one standard cc of carbon dioxide on one run. As a rule, two to three 4 standard cc natural gas samples had to be run to get one standard cc of carbon dioxide from the combustion of the propane homolog.

The vacuum extraction line used to purify and isolate the combustion products (see Figure I-19) was made principally from 9 mm OD pyrex tubing and was designed to be quite compact in order to minimize the freeze transfer path lengths. Only Ace Glass Company high vacuum teflon stopcocks were used. Purified carbon dioxide and water samples were stored in glass breakseals for C^{13}/C^{12} and D/H ratio measurements.

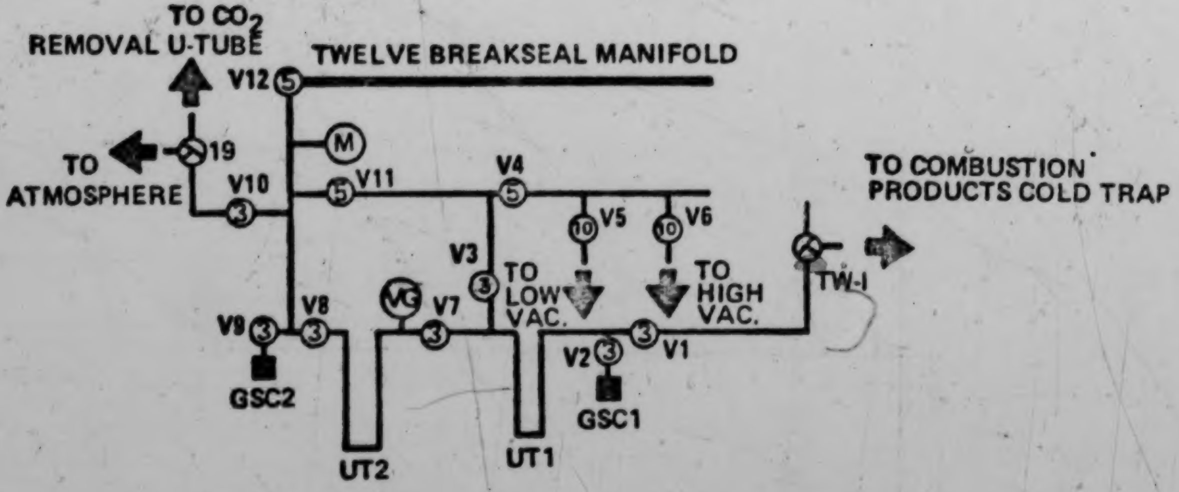
h) Carbon Isotope Reproducibility and Accuracy of the Copper (II) Oxide Combustion Furnace Method

Reproducibilities of δC^{13} values for carbon dioxide obtained from the oxidation of methane, ethane and propane using the copper oxide furnace method were estimated by pooling the standard deviations calculated from carbon isotope analyses of replicate gas sample combustions. The mathematical procedure used is outlined in books by Dixon and Massey (1969) and Johnson and Leone (1964). Table I-X lists the δC^{13} values for replicate burns of gas samples. The pooled standard deviations of carbon del values are: for methane, 0.1‰; for ethane, 0.2‰; and for propane, 0.2‰. Since only two replicate analyses were run for the ethane and propane homologs, the true reproducibility of these δC^{13} values may be higher or lower by 0.1‰.

The accuracy of the δC^{13} analyses of the gases is not well known. No interlaboratory hydrocarbon gas standard is available. However,

FIGURE I - 19

COMBUSTION PRODUCTS SEPARATION LINE


TO CO_2
REMOVAL U-TUBE
TWELVE BREAKSEAL MANIFOLD
V12
M
TO
ATMOSPHERE
19
V10
V11
V4
V5
V6
TO COMBUSTION
PRODUCTS COLD TRAP
V3
TO
LOW
VAC.
TO
HIGH
VAC.
TW-I
V9
V8
VG
V7
V2
V1
GSC2
GSC1
UT2
UT1

LEGEND

⑤ : 5 MM TEFLON HIGH VAC-STOPCOCK
GSC : GAS STORAGE CONTAINER
UT : U-TUBE COLD TRAP
M : MERCURY MANOMETER
VG : VACUUM GAUGE

TABLE I-X

CARBON ISOTOPE ANALYSES OF DUPLICATE BURNS OF METHANE, ETHANE AND PROPANE GASES

WELL NAME		$\delta C^{13}CH_4$	$\delta C^{13}C_3H_6$	$\delta C^{13}C_2H_8$
IOE Woodbend 8-5 sep. gas			-34.5‰ -34.5‰	-30.4‰ -30.6‰
GOC West Drumheller 12-1-30-21 W4M				-36.2‰ -36.0‰
HBOG Sylvan Lake		-41.2‰ -41.4‰	-32.3‰ -32.0‰	
Shell Canada Wimborne 7-26-33-26 W4M		-39.9‰ -40.1‰		
HBOG Pine Creek 10-16-		-36.6‰ -36.5‰		
HBOG Pine Creek 10-23-		-37.0‰ -37.0‰		
HBOG Pine N.W.		-33.9‰ -33.8‰		
Shell Can. Harmatten 10-11-32-3 S5M		-31.1‰ -31.2‰		
Aquitain Ricinus 7-13-36-10 W5M		-40.5‰ -40.5‰		
Aquitain Ricinus 10-33-36-10 W5M		-40.1‰ -40.1‰		
Aquitain Strachan 10-21		-36.8‰ -36.8‰		
Amoco Beaver River	#A2	-30.8‰ -31.0‰		
	#A3	-30.8‰ -30.9‰		
	#A5	-31.0‰ -31.0‰		
	#B1	-31.0‰ -31.1‰		
	#B2	-30.8‰ -30.8‰		

the carbon isotope values determined for chromatographed methane gas from the D-3 reefs along the Homeglen Rimbey-Redwater trend can be compared with values quoted by Amoco Production Research Centre, Imperial Oil Enterprises Ltd. and R. Krouse, University of Calgary. Amoco gives a value of -52.8‰ for methane separated from Redwater solution gas. Analyses of Redwater sales gas done in this thesis show a value of -53.5‰ for the δC^{13} of the methane component. Imperial Oil quotes a value of -42.6‰ for methane gas from the D-3 at Leduc. This study found values of -43.8‰, -43.6‰ and -43.5‰ for the carbon isotope values of methane gas from the adjacent Leduc reefs at Acheson, Yekau Lake and Woodbend, respectively. R. Krouse quotes values of -52‰ and -42.5‰ for the carbon del values of methane gas from the St. Albert Big Lake and Strachan D-3 reefs, respectively (see Hitchon _et_ _al_., 1975). This thesis reports δC^{13} values of -45.6‰ and -36.8‰ for methane gas from these same two D-3 reservoirs.

The agreement between the carbon isotope analyses of chromatographed methane gas and the δC^{13} values of the distilled methane component determined by Amoco and Imperial Oil is good. However, the average difference, 0.9‰, between the isotope analyses is significant. Furthermore, the chromatographed methane is more C^{12} - enriched. These facts suggest that the two procedures used to separate and combust the methane component may not be equivalent. Both Amoco and Imperial Oil distilled the methane component from a natural gas under vacuum, by circulating it through a cold trap at liquid oxygen temperatures (see Stahl, 1967). The separated methane was then mixed with oxygen and circulated through a copper oxide furnace, set at 700°C, for a period of two hours (see Stahl, 1967). Colombo et al. (1966) reports up to a 3‰ fractionation effect incurred through the incomplete recovery of a chromatographed methane gas. This effect is of an order of magnitude similar to the discrepancy between the del values determined on methane gas separated by the chromatography and distillation procedures. A more thorough comparison between the processes should be made. The reason for the considerable difference, approximately 5 per mil, between the carbon del values quoted by R. Krouse and those given in this thesis is uncertain.+ This disparity does not, however, invalidate any conclusions based on trends, since each laboratory is standardized internally. No carbon isotope values for the ethane and propane components were available for comparison. Presumably the accuracy of the δC^{13} analyses for these homologs is similar to, if not better than, that of methane.

+ A more thorough comparison of the δC^{13} values for methane gas from Homeglen-Rimbey-Redwater pools analysed for this thesis, with the data published by H. R. Krouse (see Hitchon et al., 1975 - slide 12) establishes this difference at an average value of 8 per mil. Agreement between methane carbon del values reported in this thesis and those analysed by H. R. Krouse, but not reported in Hitchon et al. (1975), was possible (H. R. Krouse personal communication).

Section 6: Procedures for the Liquid Chromatography of Oils and the Gas-Liquid Chromatography of the Saturate Fraction

a) Liquid Chromatography of Oils

Crude oil samples were separated into their asphaltene, benzene soluble asphaltene, aromatic, saturate, soluble NSO, and insoluble NSO fractions* using the procedure described by Jobson et al (1972). This method is quite similar to that used by Imperial Oil Research Laboratories, Calgary, Alberta. In this method 0.50 gram samples of crude oil were "topped" in preweighed 150 ml beakers for a period of 19 hours. The topping procedure removed the more volatile C_{15} fraction of the oil by heating the sample to 40°C in a forced draft oven. On the average, the oil samples lost between 30% and 40% of their pretopped weight and some of the high API gravity oils lost as much as 94% of this weight. Topped oil weights were generally found to be stable to within 4% over a period of 4 months. The asphaltene portion of the topped oil was precipitated by adding 10 ml of n-pentane. The pentane solubles and asphaltene precipitate were then transferred to a 1 cm x 15 cm column of Fisher Scientific Co. Hyflo Super Cel suspended in n-pentane. This column was then developed with 50 ml of n-pentane followed by 40 ml of benzene to elute, respectively, the deasphaltened oil and the benzene soluble asphaltenes (maltenes). The weight of the benzene-insoluble asphaltenes remaining on the column was calculated by difference. Forty mg or less of the deasphaltened oil was then fractionated by adsorption chromatography using a dual phase 1 cm x 40 cm column containing 10 ±0.2 g of activated 28-200 mesh Matheson silica gel in the bottom half, and 10 ±0.2 g of activated Matheson F-20 alumina gel in the upper half. Both phases were suspended in n-pentane. The pentane-deasphaltened oil solution was transferred to the top of the dual phase column using a pasteur pipette and allowed to run into the alumina gel. Any deasphaltened oil coating the column sides above the alumina gel phase was washed into the column using a small volume (approximately 5 ml) of pentane. The column was then eluted sequentially with 65 ml of pentane, 100 ml of benzene and 100 ml of a 1:1 benzene-methanol solution. Development with 65 ml of pentane was usually sufficient to completely elute the saturates from the column. However, if the pentane solution coming off the column still had significant color, further 10 ml pentane washes were necessary. The benzene and benzene-methanol solvents coming off the dual phase column contained the aromatic and NSO fractions respectively. However, a small amount of the NSO fraction was eluted by the benzene solvent. Consequently, the column was developed with no more than 100 ml of benzene. The sum of the saturate, aromatic and soluble NSO fractions subtracted from the weight of the deasphaltened oil represents the weight of the insoluble NSO component. The abundance of the various oil fractions has been reported as a percentage of the topped oil weight. In some instances the sum of the percent saturates, aromatics, NSO's and asphaltenes exceeded 100%. Two factors may have caused this. First of all, water can be incorporated into the pentane-saturate and pentane-deasphaltened oil solutions by condensation around the stopcock outlet at the base of the column, caused by cooling from pentane evaporation. This water, when incorporated into the solution, forms an immiscible phase covered with an oil film and does not easily evaporate. Second of all, the pentane, benzene and benzene-methanol solvents may not have been completely evaporated. Usually, after evaporating the solutions containing the oil fractions to dryness in a fume cabinet, a further 24 to 72 hours of vacuum desiccation gave a water and solvent free oil fraction.

---

* The NSO fraction consists of polar organic molecules containing oxygen, sulphur and nitrogen atoms.

All solvents used in the liquid chromatography of the oils were of insecticide grade and gave no interfering peaks over the C_{15} to C_{35} saturate chain length.

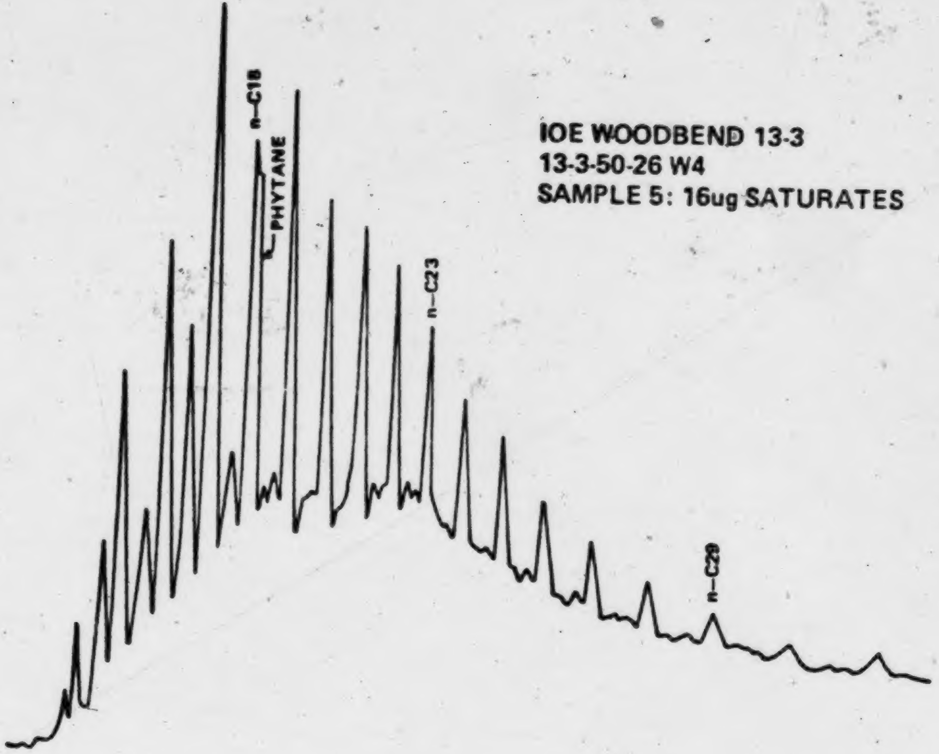
b) Gas-Liquid Chromatography of the Saturate Fraction

From 0.2 to 0.3 microlitres of a benzene-saturate solution containing 40 micrograms of saturates per microlitre was analyzed using a Varian Aerograph Chromatograph model 1740-1. The chromatograph was equipped with a flame ionization detector and a 20 foot (1/8 inch inner diameter) stainless steel column containing 5% OV-101 supported on chromosorb W. Each column was conditioned at 325°C for a period of 72 hours prior to use. All carrier gases were purified by passing them through a trap made of 5A Hydro Purge molecular sieves prior to passing them through the column or detector. To avoid the problem of carbonization of the flame ionization unit, the initial column temperature was set at 100°C and after the injection of the sample, the temperature was programmed to increase at a rate of 20°C per minute to 150°C. At this temperature the solvent peak passed through the detector. The temperature was then programmed to increase to a maximum of 300°C at a rate of 12°C per minute. The injection block temperature was set at 300°C and gas flow rates were set as follows: nitrogen carrier gas flow rate, 12.0 ml per minute; hydrogen flow rate, 15.0 ml per minute; air flow rate, 300 ml per minute.

The time of appearance of the solvent peak to the appearance of the n-C_{33} peak was approximately 25 minutes. A typical chromatogram of the saturate fraction is shown in Figure I-20. The overall outline of the chromatogram is one of n-paraffin and isoparaffin peaks, showing varying degrees of separation, perched on an approximately semicircular cycloalkane base. With the exception of the isoprenoids pristane and phytane (i-C_{17} and i-C_{18}) the isoparaffins have a subdued profile. With time, the quality of the OV-101 column degraded from exposure to the benzene solvent, and its resolving power declined to the point where pristane and phytane could no

FIGURE I - 20

SATURATE PROFILE OV-101 COLUMN



IOE WOODBEND 13-3
13-3-50-26 W4
SAMPLE 5: 16ug SATURATES

longer be resolved from their normal paraffin isomers n-C_{17} and n-C_{18}.

c) Error Calculations for the Liquid and Gas-Liquid Chromatograph Analyses

The reproducibility of the oil fraction percents was determined by pooling the best estimate of standard deviations calculated from replicate analyses of oil fractions (refer to Dixon and Massey, 1969 and Johnson and Leone, 1964). These pooled standard deviations are shown in Table I-XI.

For the less abundant oil fractions, the maltenes and NSO's, the pooled standard deviations are about 16% of an average analysis. For the more abundant saturate and aromatic fractions, their pooled standard deviations are about 4% of an average analysis. Consequently, the oil fraction analyses determined by liquid chromatography are only semiquantitative.

Chromatograms from the analysis of the saturate fraction of oils, using the OV-101 column, were compared to standard saturate profiles of biodegraded oils in order to qualitatively assess biodegradation. Therefore, an analysis of error was not done. Provided that the chromatograms were run within the same week, duplicate analyses had very similar profiles. Due to poor sample storage, duplicate analyses run a few months apart showed significant dif-

TABLE I-XI

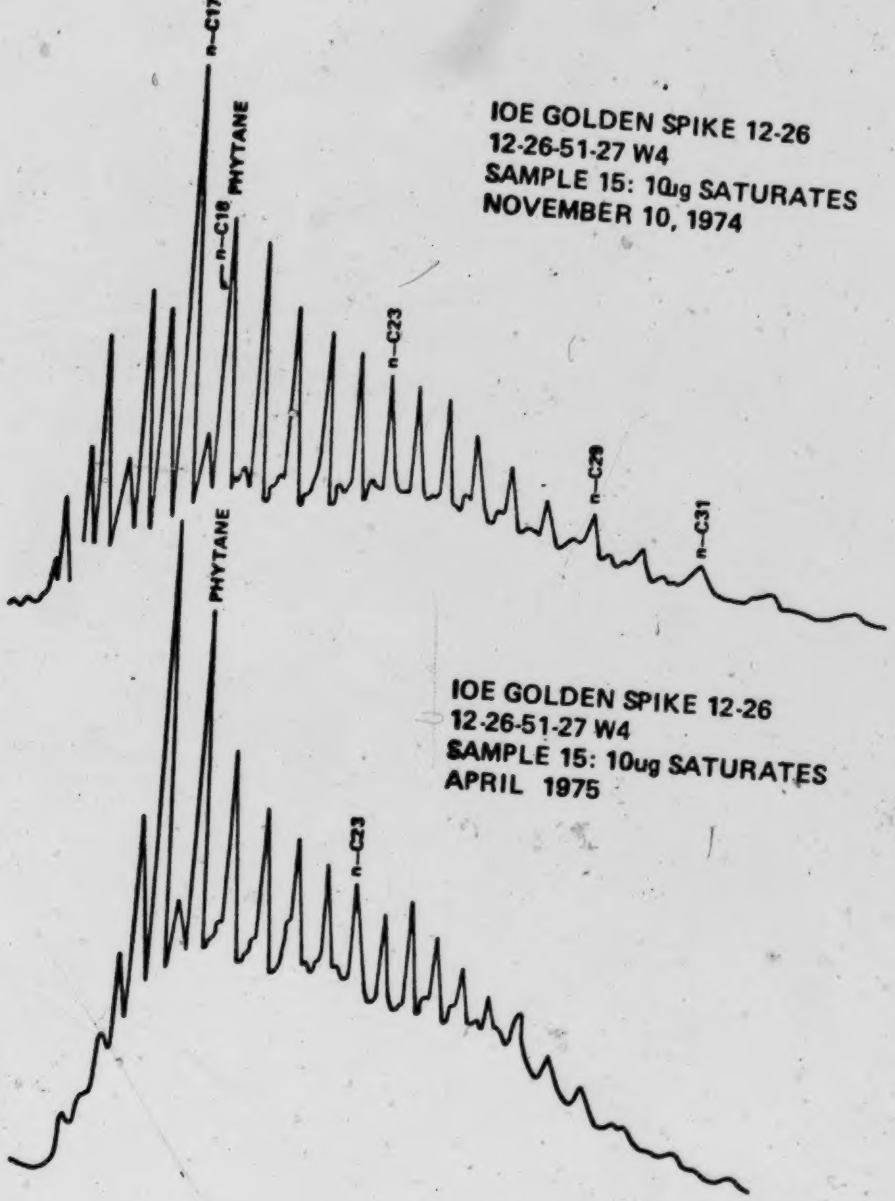
REPRODUCIBILITY OF OIL FRACTION PERCENTS DETERMINED BY LIQUID CHROMATOGRAPHY

Oil Fraction	Pooled Standard Deviation	Percentage of an Average Analysis
Saturates	1.7%	4%
Aromatics	1.4%	4%
Benzene Soluble NSO's	0.9%	12%
Maltenes	0.6%	20%

ferences. Compare A and B of Figure I-21. Later chromatograms, characterized by B, showed much more subdued n-C_{15} to n-C_{20} peaks with a near complete loss of the n-C_{13} and n-C_{14} components. It was, therefore, necessary to chromatograph the saturate fraction soon after its recovery from the dual phase column in order to preserve a continuity in the qualitative assessment of biodegradation.

FIGURE I - 21

SATURATE PROFILES



IOE GOLDEN SPIKE 12-26
12-26-51-27 W4
SAMPLE 15: 10ug SATURATES
NOVEMBER 10, 1974

IOE GOLDEN SPIKE 12-26
12-26-51-27 W4
SAMPLE 15: 10ug SATURATES
APRIL 1975

CHAPTER II

MASS SPECTROMETER CALIBRATION AND CORRECTION EQUATIONS

Section 1: Introduction

Sulphur and carbon isotope ratios were determined from sulphur dioxide and carbon dioxide gases using the University of Alberta Physics Department mass spectrometer. This instrument is a 12-inch 90° sector dual collection gas source mass spectrometer. Output from the vibrating reed electrometer amplifiers was digitized using a D.V.M.* and then stored in an on line computer. Data from alternate standard and sample readings could therefore be treated statistically by the computer, and an average uncorrected isotope ratio with its analytical error was printed out. The overall reproducibility of an analysis for both carbon and sulphur, that is the instrument error, was less than 0.1 per mil. The inlet system of this instrument was designed to prevent "cross talk" between sample and standard (Coleman and Gray, 1972). Further, peak overlap was minimal and therefore no tailing corrections between masses 64 and 65 and masses 44 and 45 were necessary.

---

*Digital Volt Meter

Section 2: Sulphur Isotope Correction and Calibration Equations*

Due to the size of the Faraday cups and the slit arrangement within the collector of the mass spectrometer, the measured sulphur dioxide beam intensity ratio, or R^{66}, is $\frac{\text{mass } 66}{\text{mass } 64 + \text{mass } 65}$. Masses 66, 65 and 64 consist of the following molecules:

64: $S^{32}O^{16}O^{16}$

65: $S^{33}O^{16}O^{16}$, $S^{32}O^{16}O^{17}$, $S^{32}O^{17}O^{16}$

66: $S^{32}O^{16}O^{18}$, $S^{32}O^{18}O^{16}$, $S^{33}O^{17}O^{16}$, $S^{33}O^{16}O^{17}$, $S^{34}O^{16}O^{16}$, $S^{32}O^{17}O^{17}$

The beam intensity ratio can be expressed in terms of its component masses-ions as:

$$R^{66} = \frac{S^{32}O^{16}O^{18} + S^{32}O^{18}O^{16} + S^{33}O^{16}O^{17} + S^{33}O^{17}O^{16} + S^{32}O^{17}O^{17} + S^{34}O^{16}O^{16}}{S^{33}O^{16}O^{16} + S^{32}O^{16}O^{17} + S^{32}O^{17}O^{16} + S^{32}O^{16}O^{16}} \qquad \text{I-1.}$$

Dividing both numerator and denominator by $S^{32}O^{16}O^{16}$, equation 1 simplifies to:

$$R^{66} = \frac{2\frac{O^{18}}{O^{16}} + 2\frac{S^{33}}{S^{32}} \cdot \frac{O^{17}}{O^{16}} + \left[\frac{O^{17}}{O^{16}}\right]^2 + \frac{S^{34}}{S^{32}}}{\frac{S^{33}}{S^{32}} + 2\frac{O^{17}}{O^{16}} + 1} \qquad \text{I-2.}$$

---

* The theoretical development of the oxygen correction equation closely follows the arguments used in the Thode Laboratory Report #42, McMaster University.

Rearranging equation 2 gives the desired sulphur isotope ratio S^{34}/S^{32} as:

$$\frac{S^{34}}{S^{32}} = R^{66}\left[1 + \frac{S^{33}}{S^{32}} + 2\frac{O^{17}}{O^{16}}\right] - \left[2\frac{O^{18}}{O^{16}} + 2\frac{S^{33}}{S^{32}} \cdot \frac{O^{17}}{O^{16}} + \left(\frac{O^{17}}{O^{16}}\right)^2\right] \qquad \text{I-3.}$$

As a result of the order of magnitude of the ratios, second order terms can be considered of negligible magnitude. Therefore, equation 3 becomes:

$$\frac{S^{34}}{S^{32}} = R^{66}\left[1 + \frac{S^{33}}{S^{32}} + 2\frac{O^{17}}{O^{16}}\right] - 2\frac{O^{18}}{O^{16}} \qquad \text{I-4.}$$

Due to factors inherent in the design of the mass spectrometer, only a value proportional to R^{66} was measured. Therefore, equation 4 must be modified to:

$$\frac{S^{34}}{S^{32}} = kR^{66}\left[1 + \frac{S^{33}}{S^{32}} + 2\frac{O^{17}}{O^{16}}\right] - 2\frac{O^{18}}{O^{16}} \qquad \text{I-5.}$$

where k is a constant which corrects for source ionization peculiarities etc. and should have a value close to unity. To avoid calculating k, each gas sample was run against a standard gas and the result expressed as a ratio of S^{34}/S^{32} values for the sample and standard. That is:

$$\frac{\left(\frac{S^{34}}{S^{32}}\right)_X}{\left(\frac{S^{34}}{S^{32}}\right)_S} = \frac{kR^{66}_X\left[1 + \left(\frac{S^{33}}{S^{32}}\right)_X + 2\left(\frac{O^{17}}{O^{16}}\right)_X\right] - 2\left(\frac{O^{18}}{O^{16}}\right)_X}{kR^{66}_S\left[1 + \left(\frac{S^{33}}{S^{32}}\right)_S + 2\left(\frac{O^{17}}{O^{16}}\right)_S\right] - 2\left(\frac{O^{18}}{O^{16}}\right)_S} \qquad \text{I-6.}$$

The subscripts X and S designate sample and standard values, respectively. Since the constant k has the same value in both numerator and denominator in equation 6, it cancels. Let the terms:

$S^{34}/S^{32} = R^{34}$

$S^{33}/S^{32} = R^{33}$

$O^{17}/O^{16} = R^{17}$

$O^{18}/O^{16} = R^{18}$

Making these substitutions and dividing by R_S^{66}, equation 6 becomes:

$$\frac{R_X^{34}}{R_S^{34}} = \frac{\frac{R_X^{66}}{R_S^{66}}[1 + R_X^{33} + 2R_X^{17}] - 2\frac{R_X^{18}}{R_S^{66}}}{1 + R_S^{33} + 2R_S^{17} - 2\frac{R_S^{18}}{R_S^{66}}} \qquad \text{I-7.}$$

The value R_X^{66}/R_S^{66} is the raw isotope measurement obtained from the mass spectrometer. Therefore, to convert the raw R_X^{66}/R_S^{66} ratio to a R_X^{34}/R_S^{34} value, it is necessary to know the R^{33}, R^{17} and R^{18} values for the sample and standard, and the R^{66} ratio for the standard. These oxygen and sulphur isotopic ratios should be known exactly for the standard, and only approximately for the sample.

R_X^{17} is related to R_X^{18} through the following equation:

$$\frac{R_X^{17}}{R_S^{17}} \quad {\frac{R_X^{18}}{R_S^{18}}}^{1/2} \qquad \text{(see Craig, 1957)} \qquad \text{I-8.}$$

R_X^{33} is related to R_X^{34} through a similar relationship:

$$\frac{R_X^{33}}{R_S^{33}} \quad {\frac{R_X^{34}}{R_S^{34}}}^{1/2} \qquad \text{(see Thode Report \#42)} \qquad \text{I-9.}$$

This can be rewritten as:

$$\frac{R_X^{33}}{R_S^{33}} = \frac{\delta S_{X-S}^{34}}{2} \tag{I-10.}$$

Where,

$$\delta S_{X-S}^{34} = \left[\frac{R_X^{34}}{R_S^{34}} - 1\right] 1000 \tag{I-11.}$$

Let,

$$1 + R_S^{33} + 2R_S^{17} - \frac{R_S^{18}}{R_S^{66}} = M \tag{I-12.}$$

Using equations 10, 11 and 12, equation 7 can be modified to:

$$\delta S_{X-S}^{34} = \frac{\frac{R_X^{66}}{R_S^{66}}\left[1 + 2R_X^{17}\right] - 2\,\frac{R_X^{18}}{R_S^{66}} - M}{\frac{M}{1000} - \frac{R_X^{66}}{2R_S^{66}}} \tag{I-13.}$$

Therefore, raw R_X^{66}/R_S^{66} ratios determined from the mass spectrometer can be corrected to δS_{X-S}^{34} values using equation 13. Depending on the mass spectrometer design and the type of inlet system used, peak tailing and inlet "cross talk" corrections may also be required (see Deines, 1970). It was not necessary to make these corrections for the instrument used in this work. In order to make interlaboratory comparisons and to report data in literature, the δS_{X-S}^{34} values (where S designates a particular laboratory standard) must be changed to del values referred to the international standard Canon Diablo troilite (CDT). This conversion is done using equations 11 and 14.

$$\delta S_{X-CDT}^{34} = \left[\frac{R_X^{34}}{R_S^{34}} \cdot \frac{R_S^{34}}{R_{CDT}^{34}} - 1\right] 1000 \tag{I-14.}$$

R_{CDT}^{34} is known precisely as 4.499437 x 10^{-2} (Thode report #42).

Considerable time was spent trying to determine the R^{17} and R^{18} values for the line standard. Several fluorination experiments were unsuccessful and educated estimates of R^{17} and R^{18} proved unsatisfactory. Consequently, raw mass spectrometer data could not be corrected using equation 13. Instead, a plot of δ^{66}_{X-S}* vs. δS^{34}_{X-CDT} was made for several NBS and laboratory sulphur standards (see Figure I-22).

A least squares best fit to the data gives the equation:

$$\delta S^{34}_{X-CDT} = 1.138\ \delta^{66}_{X-S} + 4\cdot3 \qquad \text{I-15.}$$

The error of the slope and y-intercept is 0.01 and 0.1, respectively. δS^{34}_{X-CDT} values for the laboratory standards were provided by the Thode laboratory at McMaster University. Table I-XII lists the data used in Figure I-22.

The reproducibility of the sulphur isotope analyses is given as the pooled standard deviation of replicate runs on the NBS and laboratory standards. This value is ±0.1‰, and incorporates all uncertainty which may be introduced by sample inhomogeneity, irregularities in chemical preparation and errors in mass spectrometric measurements. δ^{66} values for the Fisher ZnS standard had a much larger standard deviation, 0.4‰.

---

* $\delta^{66}_{X-S} = \left[\frac{R^{66}_{X}}{R^{66}_{S}} - 1\right] 1000$

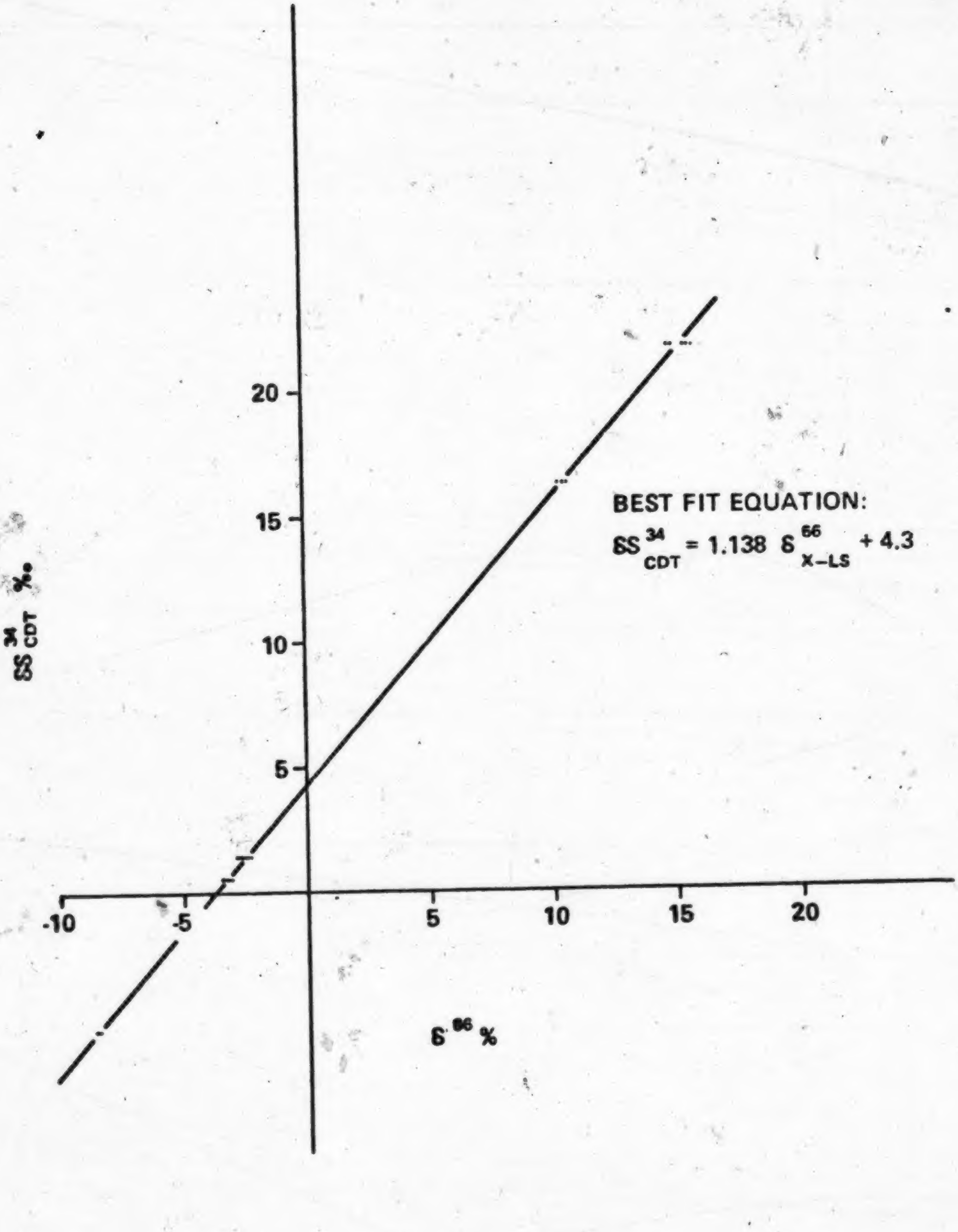
TABLE I-XII

DATA FOR THE SULPHUR CORRECTION AND CALIBRATION EQUATION

δ^{66}	δS^{34}_{CDT}				
-2.6	+1.4	-3.64	6.76	1.96	NBS 120 (PbS)
-2.8	+1.4	-3.92	7.84	1.96	$\overline{X}^{66}$ = -2.60‰
-2.7	+1.4	-3.78	7.29	1.96	N = 8
-2.7	+1.4	-3.78	7.29	1.96	S_D = 0.1‰
-2.5	+1.4	-3.50	6.25	1.96	
-2.5	+1.4	-3.50	6.25	1.96	$\overline{Y}^{34}$ = 1.4‰
-2.4	+1.4	-3.36	5.76	1.96	S_D = 0.1‰
-2.6	+1.4	-3.64	6.76	1.96	
-20.80	+11.20	-29.12	54.20	15.68	SUM
-3.3	+0.6	-1.98	10.89	0.36	NBS 200 (Sulphur)
-3.2	+0.6	-1.98	10.34	0.36	$\overline{X}^{66}$ = -3.3‰
-3.3	+0.6	-1.98	10.89	0.36	N = 9
-3.3	+0.6	-1.98	10.89	0.36	S_D = 0.1‰
-3.4	+0.6	-2.04	11.59	0.36	
-3.4	+0.6	-2.04	11.56	0.36	$\overline{Y}^{34}$ = 0.6‰
-3.4	+0.6	-2.04	11.56	0.36	S_D = 0.1‰
-3.4	+0.6	-2.04	11.56	0.36	
-3.4	+0.6	-2.04	11.56	0.36	
-30.1	+5.40	-18.06	100.71	3.24	SUM
-8.6	-5.5	+47.30	73.96	30.25	McMaster Ag_2S Standard
-8.5	-5.5	+46.75	72.25	30.25	$\overline{X}^{66}$ = -8.5‰ $\overline{Y}^{34}$ = -5.5‰
-8.5	-5.5	+46.75	72.25	30.25	S_D = 0.1‰ S_D = 0.1‰
-25.6	-16.5	+140.80	218.46	90.75	SUM
+15.6	+21.7	338.52	243.36	470.89	Fisher ZnS Standard
+15.4	+21.7	334.18	237.16	470.89	$\overline{X}^{66}$ = +15.27‰ $\overline{Y}^{34}$ = +21.7‰
+15.7	+21.7	340.69	246.49	470.89	S_D = 0.4‰ S_D = 0.2‰
+14.8	+21.7	321.16	219.04	470.89	N = 5
+14.9	+21.7	323.33	222.01	470.89	
+76.40	+108.50	1657.88	1168.06	2354.45	SUM
+10.6	+16.3	172.78	112.36	265.69	Shell Can. Wimborne Ag_2S
+10.6	+16.3	172.78	112.36	265.69	$\overline{X}^{66}$ = +10.56‰ $\overline{Y}^{34}$ = +16.3‰
+10.7	+16.3	174.41	114.49	265.69	S_D = 0.1‰ S_D = 0.1‰
+10.5	+16.3	171.15	110.25	254.69	N = 5
+10.4	+16.3	169.52	108.16	265.69	
+52.80	+81.50	860.64	557.62	1328.45	SUM
-3.5	0	0	12.25	0	Troilite
-3.5	0	0	12.25	0	$\overline{X}^{66}$ = -3.43‰ $\overline{Y}^{66}$ = 0‰
-3.3	0	0	10.89	0	S_D = 0.1‰ S_D = 0.1‰
					N = 3
-10.30	0	0	35.39	0	SUM

FIGURE I - 22

SULPHUR ISOTOPE CALIBRATION AND CORRECTION EQUATION



Such variability appeared to be the result of sample inhomogeneity. Since equation 15 is both a mass correction and calibration equation, the calculated δS^{34}_{X-CDT} values are reasonably accurate.

Section 3: Carbon Isotope Correction Equation

An oxygen correction equation for carbon isotope analyses is discussed by Craig (1957). However, the collector slit arrangement used by Craig was different from that in the mass spectrometer used for this thesis. Craig's collector gathered only ions of mass 44 and mass 45. Consequently, the measured ratio, R^{45}, had only to be corrected for an O^{17} contribution. The collector slit and Faraday cup arrangement in the University of Alberta Physics Department mass spectrometer resulted in the simultaneous collection of masses (44 + 46) and mass 45. Therefore, the measured ratio, R^{45}, had to be corrected for not only an O^{17} contribution, but also for an O^{18} contribution.

For this thesis, the measured R^{45} ratio was defined as:

$$R^{45} = \frac{\text{beam intensity of mass 45}}{\text{beam intensity of (mass 44 + mass 46)}}$$

Following Craig's 1957 derivation, R^{45} can be expressed in terms of molecular species as:

$$R^{45} = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16} + C^{12}O^{16}O^{18} + C^{12}O^{17}O^{17} + C^{13}O^{16}O^{17}} \qquad \text{I-16.}$$

Due to the extremely low abundance of O^{17}, the $C^{12}O^{17}O^{17}$ contribution to the mass (44 + 46) beam intensity need not be considered. Equation 16 then becomes:

$$R^{45} = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16} + C^{12}O^{16}O^{18} + C^{13}O^{16}O^{17}} \qquad \text{I-17.}$$

Dividing both the numerator and denominator of equation 17 by $C^{12}O^{16}O^{16}$ gives:

$$R^{45} = \frac{\dfrac{C^{13}O^{16}O^{16}}{C^{12}O^{16}O^{16}} + \dfrac{C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16}}}{1 + \dfrac{C^{12}O^{16}O^{18}}{C^{12}O^{16}O^{16}} + \dfrac{C^{13}O^{16}O^{17}}{C^{12}O^{16}O^{16}}} \qquad \text{I-18.}$$

The following ratios were defined after Craig, 1957:

$$R^{13} = \frac{C^{13}}{C^{12}} \ ; \quad R^{18} = \frac{O^{16}O^{18}}{O^{16}O^{16}} \ ; \quad R^{17} = \frac{O^{16}O^{17}}{O^{16}O^{16}} \ ; \quad \text{and } R^{13}.R^{17} = \frac{C^{13}O^{16}O^{17}}{C^{12}O^{16}O^{16}}$$

Substituting these terms into equation 18, it becomes:

$$R^{45} = \frac{R^{13} + R^{17}}{1 + R^{18} + R^{13}.R^{17}} \qquad \text{I-19.}$$

Rearranging equation 19 gives:

$$R^{13} = R^{45}\,[1 + R^{18} + R^{13}.R^{17}] - R^{17} \qquad \text{I-20.}$$

Since the magnitude of the term $R^{13}.R^{17}$ in equation 20 is around $1\text{x}10^{-5}$, and R^{13} is approximately $1\text{x}10^{-2}$, the former term can be omitted without any serious loss of accuracy to the R^{13} value. Therefore, equation 19 can be written as:

$$R^{45} = \frac{R^{13} + R^{17}}{1 + R^{18}} \qquad \text{I-21.}$$

Since the isotopic measurements are made relative to a standard, equation 21 must be modified to:

$$\frac{R_X^{45}}{R_S^{45}} = \frac{\dfrac{R_X^{13} + R_X^{17}}{1 + R_X^{18}}}{\dfrac{R_S^{13} + R_S^{17}}{1 + R_S^{18}}} \qquad \text{I-22.}$$

The subscripts S and X designate the standard and sample, respectively. Values for R^{13}, R^{17} and R^{18} were known precisely and the denominator in equation 22 is therefore a constant which is termed K" in the following equation.

$$\frac{R_X^{45}}{R_S^{45}} = \left[\frac{R_X^{13} + R_X^{17}}{1 + R_X^{18}}\right] \frac{1}{K''} \qquad \text{I-23.}$$

Rearranging terms, equation 23 becomes:

$$R_X^{13} = K''(1 + R_X^{18})\frac{R_X^{45}}{R_S^{45}} - R_X^{17} \qquad \text{I-24.}$$

R^{18} can be approximated from the measured ratio R_X^{46}/R_S^{46} without any serious error. R^{17} can be derived from the relationship that:

$$\frac{R_X^{17}}{R_S^{17}} = \left[\frac{R_X^{18}}{R_S^{18}}\right]^{1/2}$$

(Craig, 1957)

I-25.

Making the substitution that $\frac{R_X^{18}}{R_S^{18}} \simeq \frac{R_X^{46}}{R_S^{46}}$ into equation 25 gives:

$$\frac{R_X^{17}}{R_S^{17}} \simeq \left[\frac{R_X^{46}}{R_S^{46}}\right]^{1/2} \qquad \text{I-26.}$$

It should be noted, at this point, that the terms R^{17} and R^{18} used in this derivation are not eqivalent to the currently used R^{17} and R^{18} terminology.

That is: $R^{18}_{\text{Craig}} = \frac{O^{18}O^{16}}{O^{16}O^{16}} \neq \frac{O^{18}}{O^{16}} = R^{18}_{\text{current usage}}$

and $R^{17}_{\text{Craig}} = \frac{O^{17}O^{16}}{O^{16}O^{16}} \neq \frac{O^{17}}{O^{16}} = R^{17}_{\text{current usage}}$

In fact, $\frac{O^{18}O^{16}}{O^{16}O^{16}} = 2\frac{O^{18}}{O^{16}}$ and $\frac{O^{17}O^{16}}{O^{16}O^{16}} = 2\frac{O^{17}}{O^{16}}$ (Garlick, 1969)

Values of R^{17} and R^{18}, as defined by Craig (1957) for the Physics department carbon dioxide line standard are listed in Table I-XIII.

R^{17} and R^{18} values for the sample gases varied depending on the method used to oxidize the hydrocarbon. However, the standard deviation associated with mean R^{17} and R^{18} values for carbon dioxides derived from a specific oxidation method was generally small enough to permit the use of mean R^{17} and R^{18} values in the oxygen correction equation. The mean R^{17} and R^{18} values for carbon dioxide gas produced from the oxidation of oil components and natural gases using CuO and for carbon dioxide derived from the wet oxidation of whole oils using the liquid method are

TABLE I-XIII

AVERAGE R^{13}, R^{17} AND R^{18} VALUES FOR STANDARD GASES AND OXIDATION REAGENTS

Gas Description	R^{13+}	R^{17+}	R^{18+}
U of A Physics Dept. CO_2 standard	1.07043×10^{-2}	7.441×10^{-4}	3.987×10^{-3}
CO_2 derived from CuO oil oxidation	---	7.550×10^{-4}	4.105×10^{-3}
CO_2 derived from natural gas oxidation	---	7.522×10^{-4}	4.074×10^{-3}
CO_2 derived from the wet oxidation of oils	---	7.478×10^{-4}	4.027×10^{-3}
CO_2 derived from the H_3PO_4 treatment of PDB carbonate standard	1.12372×10^{-2}	7.599×10^{-4}	4.158×10^{-3}
CO_2 derived from the H_3PO_4 treatment of SF carbonate laboratory standard	1.12001×10^{-2}	7.549×10^{-4}	4.103×10^{-3}
CO_2 derived from the H_3PO_4 treatment of EDS carbonate laboratory standard	1.12192×10^{-2}	7.520×10^{-4}	4.072×10^{-3}

+ As defined by Craig, 1957.

given in Table I-XIII. The standard deviation for the mean δO^{18} values for carbon dioxides derived from oils and gases oxidized by black copper oxide using the Carius tube and furnace oxidation methods was the same, about 3 per mil. Since mean R^{17} and R^{18} values were used in the oxygen correction equations, this 3 per mil standard deviation would produce a further uncertainty in the δC^{13}_{PDB} values of approximately 0.1‰. The standard deviation of δO^{18} values for carbon dioxides prepared by the the wet oxidation method was considerably larger, approximately 7‰. By using the mean R^{17} value in the oxygen correction equation for these oil carbon dioxides, this 7‰ uncertainty would produce about a 0.2‰ error in addition to the 0.1‰ instrument error.

The following equations were used to correct raw δ^{45} values to δC^{13} values quoted with respect to the Chicago PDB standard.

1. Carius tube oxidation method oxygen correction equation:

$$\delta C^{13}_{X\text{-}PDB} = 1018.91 \frac{R^{45}_{X}}{R^{45}_{UALS}} - 1067.19$$

2. CuO furnace combustion method oxygen correction equation:

$$\delta C^{13}_{X\text{-}PDB} = 1018.88 \frac{R^{45}_{X}}{R^{45}_{UALS}} - 1066.94$$

3. Wet oxidation method oxygen correction equation:

   Carbon dioxides prepared by the wet oxidation method were analysed using the mass spectrometer of the University of Waterloo in Ontario. The oxygen correction equations derived were similar to that given by Craig (1957), which is:

$$\delta C^{13}_{X\text{-}PDB} = 1.0676 \quad ^{45} - 0.0338\, \delta O^{18}$$

The uncertainty in a δC^{13} analysis can be represented by an equation that involves the sum of the mass spectrometer error, and the variability in the C^{12}/C^{13} and O^{18}/O^{16} ratios due to the preparation procedure. To a first approximation this uncertainty is the sum of the computed standard deviation of one analysis (instrument error) plus the standard deviation associated with the average R^{18} value, both propagated through oxygen correction equation (Baird, 1962). However, the best estimate of the overall uncertainty in a δC^{13} value associated with a particular oxidation method would be the reproducibility, that is, the standard deviation of δC^{13} analyses of many carbon dioxides prepared from one large homogenous oil or natural gas sample. In this thesis, the best estimate of the reproducibility was determined by pooling the standard deviations from replicate δC^{13} analyses of different hydrocarbon samples prepared by the same oxidation method. The pooled standard deviation for δC^{13} analyses associated with the Carius tube oxidation method, the CuO furnace combustion procedure and the wet oxidation technique is 0.2‰, 0.1‰ and 0.2‰, respectively. A further discussion of error in δC^{13} values and a discussion of their accuracy can be found in Chapter I-I in the sections where each hydrocarbon procedure is presented.

PART II

THE GEOCHEMISTRY OF HYDROCARBONS IN THE DEVONIAN OF ALBERTA

CHAPTER I

INTRODUCTION - THE LEDUC REEF SYSTEM, SAMPLE PROGRAMME AND OIL SULPHURIZATION REACTIONS

Section 1: Geology and Geochemistry of the Leduc Reef System

A summary of the geology of the D-3 reefs is presented in the publication by McCrossan and Glaister (1964). Other useful papers on the Leduc system can be found in Clark (1954), in Oswald (1967) and in the publication by Davies (1975). The following is a brief summary of the Leduc system based on the above literature.

The oil bearing Leduc reefs in central Alberta form a part of a carbonate shale sequence which was deposited during an Upper Devonian transgression that began at the onset of Beaverhill Lake deposition and continued until the end of Ireton shale time.

The Cooking Lake Formation from which the Leduc, or D-3, reefs grew is a broad shallow-water carbonate platform which extends from Montana, northwards and westwards into central Alberta and merges further to the north with the Grossmont Formation. The Cooking Lake is approximately 200 ft. thick in the study area, between the Rimbey-Meadowbrook and Stettler-Big Valley D-3 reef chains (see Figure II - 1), and it thickens to the south forming a reefal carbonate, the Cairn, which attains a thickness of up to 600 ft.. Laterally the Cooking Lake grades into the shales and shaly carbonates of the Duvernay and the equivalent Perdrix Formations. Cooking Lake deposition occurred in relatively shallow water, and consisted of bedded aphanitic, fine- and medium-grained limestones and thin stromatoporoid - rich beds which formed mainly biostromes as well as bioherms. Where the biostromal and biohermal zones grew large enough to form shoals, they became the loci for later Leduc reef growth. Several prominent shoals, which probably mark an eastward prograding Cooking Lake bank-shale basin margin, localized the growth of the D-3 reefs along the Rimbey-Meadowbrook reef chain; the Bashaw carbonate bank and its northern extension, the Malmo-New Norway-Duhamel-Erskine reef chain; the Wimborne-Three Hills reef chain and the Stettler-Big Valley D-3 reef trend (see Figure II - 1). To the south and southeast of the Stettler-Big Valley D-3 trend, the interreef shaly facies passes into the southern Alberta shelf carbonate facies.

The Redwater D-3 reef is a complex structure in which three vertical zones can be recognized (Klovan, 1964 - see also Figure II - 2). The lowermost unit, or root zone, is the Cooking Lake shoal equivalent and is roughly 300 ft. thick. The Middle Leduc unit is around 500 ft.

FIGURE 11-1

LEDUC REEF DISTRIBUTION

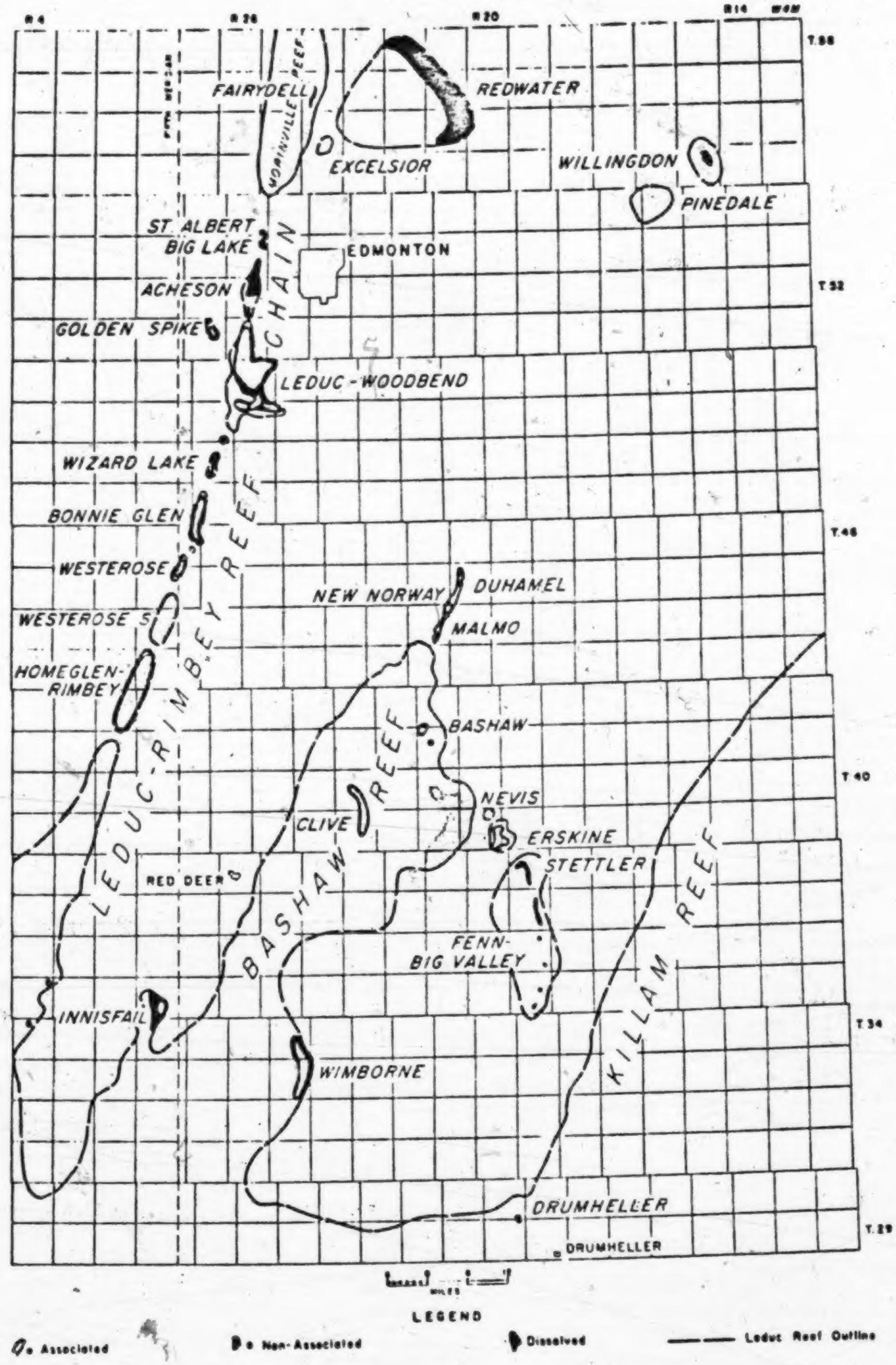
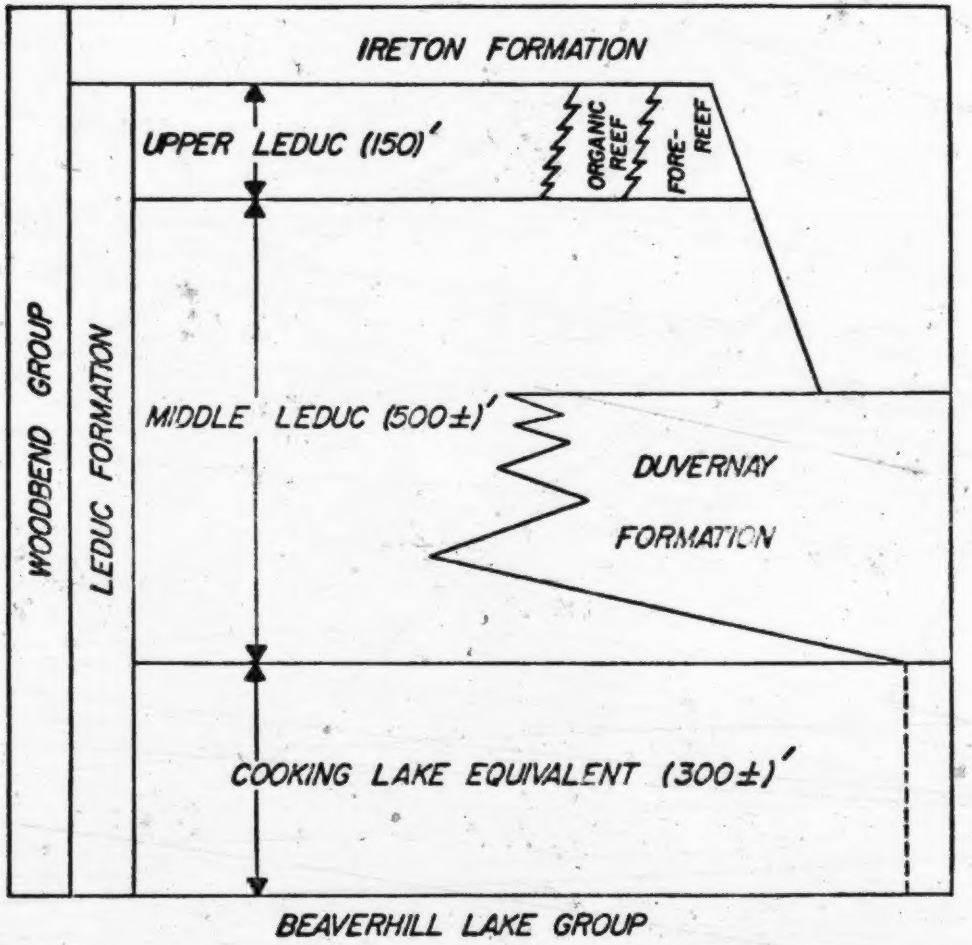

R 4
R 26
R 20
R 14
W4M
T.58
T.52
T.46
T.40
T.34
T.29
5TH MERIDIAN
FAIRYDELL
MORINVILLE REEF
REDWATER
EXCELSIOR
WILLINGDON
PINEDALE
ST. ALBERT
BIG LAKE
EDMONTON
ACHESON
GOLDEN SPIKE
CHAIN
LEDUC-WOODBEND
WIZARD LAKE
BONNIE GLEN
WESTEROSE
WESTEROSE S
HOMEGLEN-RIMBEY
LEDUC-RIMBEY REEF
NEW NORWAY
DUHAMEL
MALMO
BASHAW
BASHAW REEF
NEVIS
ERSKINE
STETTLER
CLIVE
RED DEER
FENN-BIG VALLEY
KILLAM REEF
INNISFAIL
WIMBORNE
DRUMHELLER
DRUMHELLER
MILES
LEGEND
Associated
Non-Associated
Dissolved
Leduc Reef Outline

FIGURE II - 2


IRETON FORMATION
UPPER LEDUC (150)'
ORGANIC REEF
FORE-REEF
WOODBEND GROUP
LEDUC FORMATION
MIDDLE LEDUC (500±)'
DUVERNAY FORMATION
COOKING LAKE EQUIVALENT (300±)'
BEAVERHILL LAKE GROUP

SUBDIVISIONS OF LEDUC FORMATION

thick and records both carbonate development as well as a Duvernay shale influx. None of the Upper Leduc reef zones can be recognized in this unit. The Upper Leduc unit is an algal-stromatoporoid-coral-calcarenite composite in which organic-reef, fore-reef and back-reef facies have developed (Klovan, 1964). This upper unit is approximately 150' thick.

As the Upper Devonian transgression progressed, Leduc reef development was terminated by an influx of the Ireton green shales which form the cap rock of the D-3 oil and gas pools.

The D-3 reef chains in central Alberta can be grouped into three hydrodynamic systems separated by aquitards (Hitchon, 1969a, 1969b; Alberta Oil and Gas Conservation Board Report #70-22, 1970). These three systems probably result from communication between D-3 reefs through the underlying dolomitized Cooking Lake shoals which have regional extent. The intershoal areas are low porosity, impermeable Cooking Lake pelmicrites and fine-medium grained bedded limestones which grade into anhydritic dolomites further to the south and east. The lowest and highest fluid potential systems are the Rimbey-Meadowbrook reef trend, including the Redwater D-3, and the Stettler-Big Valley reef chain respectively. An intermediate system comprised of the Bashaw-Duhamel reefs including the Wimborne-Three Hills trend is also recognized. In this thesis the three hydrodynamic systems are referred to as the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West

Drumheller reef trends following, in general, the terminology used in the Alberta Oil and Gas Conservation Board Report #70-22 (1970).

The mean, range and standard deviation for net pay thickness, average porosity, average maximum permeability, average water saturation and productive pool area for 18 Leduc reef pools are summarized in Table II - I. The pay thicknesses and productive areas have skewed frequency distributions with the assymetry towards the higher values. Leduc reservoirs contain roughly 51% of recoverable oil reserves found in Alberta prior to December 31, 1959. The largest Leduc oil pool discovered to date is Redwater which contains approximately 700,000,000 stock tank barrels of recoverable oil.

Papers discussing the geochemistry and occurrence of D-3 natural gases have been published by Hitchon (1963a, 1963b, 1964, 1968), Shaw (1967) and Prather and McCourt (1968). Deroo et al. (1977) published a geochemical study on oils in the Western Canada Sedimentary Basin which identified the source rocks of the D-3 oils to be the marine Ireton and Duvernay shales. Except for the pioneering work on the sulphur isotopes of the Cretaceous, D-2 and D-3 oils, associated gases and formation waters by Thode et al. (1958) nothing more had been published on the stable isotopes of the Leduc system when this thesis was initiated. Subsequently, papers and abstracts by Orr (1975), Burnie (1975) and Hitchon et al. (1975) documented the effect of maturation on the sulphur and carbon isotopes of D-3 natural gases. More recently

Krouse (1977) has published a summary paper in which the sulphur isotopes of the Leduc natural gases are discussed with reference to the processes of inorganic and bacterial sulphate reduction. Literature on the geochemistry of the Leduc formation waters has been published by Hitchon (1964), Hitchon and Friedman (1969), Hitchon _et_ _al_. (1971) and Van Everdingen (1968). The relationship between hydrocarbon occurrences and formation waters was investigated by Hitchon and Horn

TABLE II - I

Reservoir Statistics for D-3 Pools (Grand Averages)

	Mean	Standard Deviation	Range
Net Pay Thickness	102 ft.	126 ft.	9 ft. (Bashaw) to 478 ft. (Golden Spike)
Average Porosity	8%	2%	4.5% (New Norway) to 10.8% (Big Lake)
Maximum Permeability	753 md	431	115 (New Norway) to 1,938 md (Westerose)
Average Water Saturation	17%	7%	6% (Bonnie Glen) to 35% (Golden Spike)
Productive Area	6,164 Ac	9,983 Ac	140 Ac. (New Norway) to 37,040 (Redwater)

(1974). The authors found that waters associated with producing and non-producing wells were different, in a multivariate sense, and could be distinguished with a 95% certainty.

Section 2: Sample Locations

Oil and gas samples were taken from wellhead (where possible) from the following Leduc and Keg River pools: Acheson (AS), Bashaw (BW), Big Lake (BL), Bonnie Glen (BG), Buffalo Lake (BK), Clive (CV), Erskine (ER), Glen Park (GP), Golden Spike (GS), Leduc Woodbend (WB), Malmo (MM), New Norway (NN), Stettler (ST), Sylvan Lake (SL), West Drumheller (WD), Westerose (WR), Wimborne (WM), Wizard Lake (WL), Yekau Lake (YL); Zama Keg River 6-23-116-4 W6 (KR 6), 7-7-116-5 W6 (KR 7), 4-36-116-6 W6 (KR 4), 12-21-117-4 W6 (KR 12), 2-25-117-5 W6 (KR 2); Virgo Keg River 4-6-115-5 W6 (KR 46), 5-11-115-5 W6 (KR 51), 5-27-114-5 W6 (KR 52); and Rainbow Keg River 8-32-111-7 W6 (KR 8). Coproduced water samples were collected only from pools at Zama (KR 12), Erskine, West Drumheller, Bashaw and New Norway. Non-associated gases were sampled from the D-3 at Harmattan (HN), Pine Creek (PC), Pine Northwest (PN), Ricinus (RC), Strachan (SN) and from the Nahanni formation (Lower Keg River equivalent) at Beaver River in northeastern British Columbia. The bracketed letters after each pool name are abbreviations used to reference the pools in many of the diagrams of this thesis. With the exception of Beaver River (coordinates 59°58' N. Lat., 124°17' W. Long.) the coordinates of the above listed pools can be referenced in enclosure 1a and the pools located on enclosure 1b.

Section 3: An Introduction to the Petroleum Sulphur System

The work of the American Petroleum Institute Research Project #48 has resulted in the isolation and identification of many of the classes of, and many of the individual sulphur compounds in crude oil fractions boiling below 250°C. Research reported by Dean and Whitehead (1967), Thompson et al. (1965) and Bestougeff and Jolly (1967) discusses the sulphur compounds in the higher boiling fractions of crude oils and shale oils. More recent reviews of petroleum sulphur compounds have been prepared by Drushel (1970) and Mehmet (1971). In a summary by Speers and Whitehead (1969) the following sulphur compound groups have been identified in crude oils: native sulphur, restricted to crude oils whose temperatures were less than about 100°C; thiols, most abundant in oil fractions boiling below 150°C, thiaalkanes and cycloalkylthiaalkanes, of minor importance in this boiling range; thiacycloalkanes, bi and tricyclothiaalkanes and thiophenes (most abundant in distillate fractions boiling up to 250°C); and benzothiophenes, abundant in fractions boiling above 250°C. Except for the thienothiophenes and simple alkyl-disulphides few other sulphur compounds containing two sulphur atoms per molecule have been identified. General structures for the various organo-sulphur groups and structures for specific sulphur compounds are illustrated in Speers and Whitehead (1969), Mehmet (1971) and Ho et al. (1974). To date, there have been more than 200 oil sulphur compounds identified and these fall into some 13 classes.

According to Ho et al. (1974) the types of sulphur compounds associated with a crude oil depend on its state of organic metamorphism (refer to Staplin, 1969 and Evans et al. 1971). From a statistical treatment of a world wide sample population of crude oils, the authors concluded that immature oils were characterized by greater contents of the relatively unstable sulphur compounds such as nonthiophenic sulphides and benzothiophenes. Mature crudes were marked by an abundance of the more stable sulphur compounds such as dibenzothiophenes and lesser amounts of the unstable nonthiophenic organo-sulphides. One group of high gravity mature crudes was associated with substantial amounts of thermally generated hydrogen sulphide and lay adjacent to reservoirs containing thermally metamorphosed hydrocarbons. Although the total sulphur content of the group was low, its sulphur compounds were characterized by an abundance of the reactive mercaptans. The "altered" crude oils contained a sulphur compound distribution intermediate to the mature and immature groups.

In natural gases, the dominant sulphur compounds are hydrogen sulphide and various polysulphides (Hyne, 1968; Muller and Hyne, 1969 and Swift, 1976). Other sulphides such as COS, CS_2 and mercaptans do occur but they are not abundant. For example, Hyne (personal communication) reports less than 0.05% COS and CS_2 contents for Alberta natural gases. Vredenburg and Cheney (1971) report similar low abundances for thiols, alkyl sulphides, carbon disulphide and carbonyl sulphide in Wind River basin natural gases.

Total sulphur contents within crude oils and natural gases are variable. Levorsen (1967) and Ho et al. (1974) report a range in sulphur content in petroleum from 0.01% to 8%. Sulphur contents within heavy oils and asphalts can exceed 8%. In natural gases the sulphur content, as volume percent hydrogen sulphide, ranges from nil, to trace, to 86% in some of the thermally metamorphosed reservoirs in the foothills belt of the Albertan cordillera. Generally, natural gases containing more than 1 vol. % hydrogen sulphide are classed as sour gases. Crude oils whose sulphur content exceeds 0.5% are classed as high sulphur oils, while crudes with sulphur less than 0.5% are classed as low sulphur oils. The petroleums studied for this thesis fall into both of these groups. Crude oils sampled from the Homeglen-Rimbey-Redwater D-3 reefs are without exception low sulphur oils, while crudes from the D-3 reefs along the Wimborne-Duhamel and Stettler D-3 reef trends are both high and low sulphur oils having a maximum sulphur content of about 3% (refer to Table II - II; White, 1960 and Century, 1966). Natural gases studied for this thesis were both sweet and sour having a maximum hydrogen sulphide content of 52% (refer to Table II - II).

The reaction of sulphur compounds with hydrocarbons is essentially an oxidation process. Elemental sulphur can abstract hydrogen from organic compounds producing fragments which ultimately give stable products by aromatization, ring closure or dimerization (Pryor, 1962). The oxidation of the organic substrate is balanced by the reduction of

TABLE II - II

Selected Leduc Reef Solution Gas Analyses (From White, 1960).

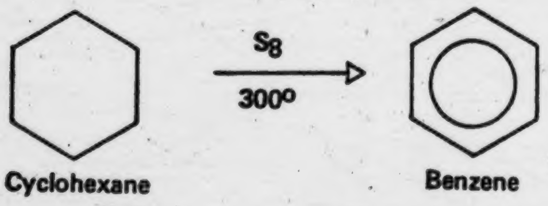
	POOL								
Component	Acheson	Big Lake	Bonnie Glen	Glen Park	Golden Spike	Leduc Woodbend	Wizard Lake	Westerose	Bashaw
Hydrogen	-	-	-	-	-	-	-	-	-
Methane	62.6	55.53	68.1	66.6	58.22	61.3	62.80	62.03	62.99
Ethane	15.4	13.26	13.8	15.2	18.00	17.6	17.07	17.02	8.45
Propane	11.2	12.27	7.1	10.4	15.15	10.9	11.95	9.30	5.83
i Butane	1.0	1.25	1.1	0.8	1.57	1.4	1.30	1.76	0.68
n Butane	2.5	2.62	2.8	2.7	4.31	2.8	3.80	3.39	2.33
Pentanes +	1.0	1.12	1.3	1.3	2.09	1.6	1.84	1.99	1.42
Nitrogen	5.2	8.93	4.5	2.3	0.00	3.5	1.24	1.71	4.82
Helium	-	-	-	-	-	-	-	-	-
Carbon Dioxide	1.1	3.96	1.0	0.7	0.66	0.9	0.00	0.96	1.63
Hydrogen Sulphide	0.0	1.06	0.3	0.0	0.00	0.00	0.00	1.84	11.83
Oil Sulphur	0.14%	0.40%	0.21%	0.20%	0.24%	0.29%	0.21%	0.30%	0.81%

TABLE II - II (Cont'd)

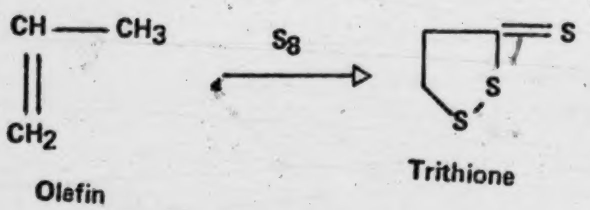
Selected Leduc Reef Solution Gas Analyses

	POOL							
Component	Clive	Erskine	Buffalo Lake	Malmo	New Norway	Stettler	West Drumheller	Wimborne
Hydrogen	-	-	0.0	-	-	-	-	0.0
Methane	60.34	66.94	56.20	63.77	59.93	51.57	68.79	65.56
Ethane	7.73	7.95	9.29	12.65	16.90	12.16	6.76	3.46
Propane	6.03	5.16	6.43	7.35	9.70	11.12	4.07	2.16
i Butane	0.85	0.81	0.88	0.75	1.07	1.48	0.66	0.41
n Butane	2.03	2.00	2.02	2.38	2.32	2.63	1.12	1.19
Pentanes +	1.34	1.40	1.21	1.48	1.37	0.90	0.44	1.77
Nitrogen	8.98	5.96	3.37	5.64	3.77	6.19	12.98	7.65
Helium	-	0.08	0.01	-	-	-	-	-
Carbon Dioxide	0.47	2.46	1.82	2.24	3.96	10.34	4.64	1.91
Hydrogen Sulphide	12.23	7.24	18.77	3.71	0.98	3.61	0.41	15.79
Oil Sulphur	0.35%	1.89%	2.44%	0.53%	1.12%	1.81%	0.99%	0.96%

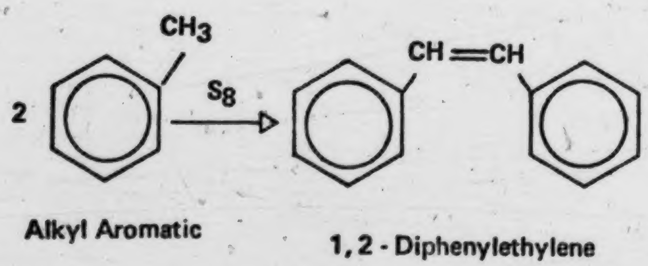
sulphur to hydrogen sulphide. Depending on the completeness of the oxidation reaction, sulphur may become incorporated into the hydrocarbon products. Pryor (1962) gives several examples of dehydrogenation reactions by elemental sulphur, for example:


S8
300°
Cyclohexane
Benzene

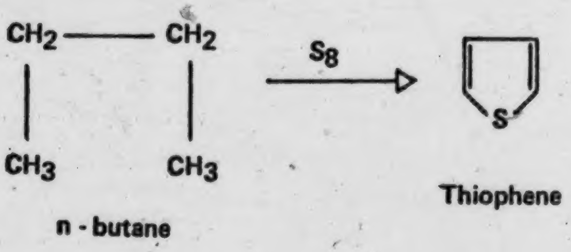
(Aromatization)


CH — CH3
CH2
Olefin
S8
S
S
S
Trithione

(Trithione Formation)

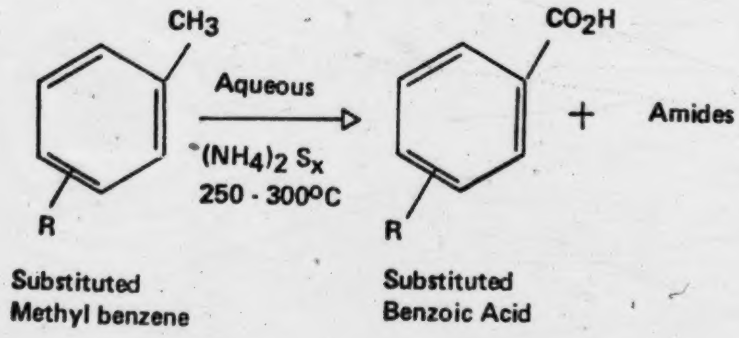

2
CH3
S8
CH ═ CH
Alkyl Aromatic
1, 2 - Diphenylethylene

(Dimerization)


CH2 — CH2
CH3
CH3
n - butane
S8
S
Thiophene

(Thiophene Formation)

Some other general hydrocarbon-sulphur reactions are given by Orr (1974). Rates of the hydrocarbon oxidation process using aqueous sulphur compounds are temperature and pH dependent. Faster reaction rates are favored by higher temperatures and increased hydrogen ion contents. At temperatures of 200-300°C uncatalysed hydrocarbon oxidations by sulphur compounds are rapid. These are not realistic reservoir temperatures in most petroliferous sedimentary basins and reactions in the natural milieux will therefore be slower and less complete. Polysulphide oxidants, such as sulphanes (H_2S_x), are capable of oxidising saturated aliphatic and alkylaromatic hydrocarbons to carboxylic acids. In the following example a substituted methyl aromatic is oxidised to a carboxylic acid and amides using an aqueous ammonium polysulphide solution:



At temperatures lower than those required for complete oxidation, organo-sulphur compounds can be isolated from polysulphide reactions (Pryor, 1962).

Experiments by Bestougeff and Combaz (1973) showed that the sulphurization of petroleum is chemically possible at all stages of its formation and entrapment. The reaction of sulphur and especially hydrogen sulphide with petroleum compounds, was found to be quite selective, and therefore the degree of sulphurization would be quite variable and dependent on the crude oil composition. During the sulphurization of crude oil by hydrogen sulphide, elemental sulphur was formed and could then react further with the petroleum compounds. Natural catalysts such as shales and montmorillonite enhanced the sulphur reactions which were performed at temperatures in the range of 50 to 100° Celsius over reaction times of 5 to 6 hours. The authors found that the heavy distillation residues of crude oils were the most easily sulphurized compounds due to their high contents of heteroatomics. Presumably their high reactivity to sulphur is a result of the low activation energies associated with a simple exchange of N or O atoms for S. Gousseva and Faingerch (1973) noted that the secondary sulphurization of crude oils produced regular changes in their composition. For example, asphaltene contents were increased, a high asphaltene to resin ratio was noted, the oily portion had an increased content of aromatics and the API gravity of the crude was decreased.

Experimental work on the Hydrocarbon-Sulphate-Reduced sulphur species system by Toland (1960) gives considerable insight into the petroleum reservoir sulphurization process. Toland reaffirmed that organic compounds including saturated hydrocarbons could be oxidised to carboxylic acids by lower valence state sulphur compounds such as elemental S (S_8), aqueous polysulphides (HS_n^-, S_n^{-2}, H_2S_n) sulphite (SO_3^{-2}) and thiosulphate ($S_2O_3^{-2}$). However, he noted that these aqueous oxidation reactions were interrelated and that the following equilibrium constant could be written to express their dependence: $K = (H_2S)^3\ (SO_4^{-2})\ (H^+)^2$. This constant corresponds to the general reaction:

$$4S^\circ + 4H_2O \rightleftharpoons 3H_2S + H_2SO_4 \qquad \text{II - 1}$$

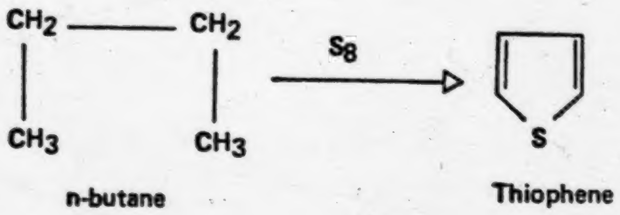
Polysulphide, sulphur, sulphite and thiosulphate oxidations were therefore found to be dependent on the pH and hydrogen sulphide concentration. Furthermore, sulphate, according to reaction II - 1, could act as an oxidising agent. Toland found that sulphate alone would not oxidise organic matter over the time span of his experiments. But, through a reaction like equation II - 1 lower valence state sulphur compounds could reduce sulphate to compounds such as sulphite and thiosulphate which would then oxidise the organic matter. The products of the oxidation were generally carboxylic acids, carbon dioxide and some other lower valence state sulphur compounds such as elemental sulphur and hydrogen sulphide or other related sulphides and polysulphides. According to equation II - 1 lower pH's and higher partial pressures of hydrogen sulphide (lower valence state sulphur compound) favor sulphate reduction and the formation of reduced sulphur species. Furthermore, any one of the lower valence state sulphur compounds formed by the reduction of sulphate and/or the concomitant oxidation of hydrocarbon could rereact with sulphate regenerating the reduction process. The reaction then is (as Toland noted) similar to being autocatalytic. His sulphate reductions and hydrocarbon oxidations were done in an aqueous medium at temperatures around 300°C. At temperatures below 300°C reactions were extremely slow. But in terms of geological time, lower temperature oxidations would certainly be significant (Toland, 1960).

Implicit in the hydrocarbon oxidation reaction using sulphate, as described by Toland (1960), are two steps: the initiation; and the oxidation. In the initiation reaction sulphate is reduced by a lower valence state sulphur species producing an oxygenated reduced-valence state sulphur compound. A possible initiation reaction is:

$$SO_4 + 2H^+ + H_2S \longrightarrow \underset{\displaystyle H_2SO_3 + S^\circ}{\underset{\upharpoonleft\downharpoonright}{H_2S_2O_3}} + H_2O \qquad \text{II - 2 Toland (1960)}$$

The second step, the oxidation, involves the reaction of sulphite or thiosulphate and elemental sulphur from reaction II - 2 with hydrocarbon, producing carboxylic acids, carbon dioxide, organo-sulphur compounds, aromatics and sulphides. Examples of the oxidation reaction are:

$$2H^+ + \underset{\text{(n-paraffin)}}{C_nH_{2n+2}} + \underset{\text{(sulphite)}}{H_2SO_3} \longrightarrow \underset{\text{(fatty acid)}}{C_{n-1}H_{2n-1}COOH} + H_2O + H_2S.$$



Toland concluded his 1960 paper by alluding that the initiation and oxidation reactions could be responsible for the generation of sour gases and high sulphur crude oils in the reservoir system.

CHAPTER II

GEOCHEMISTRY OF D-3 OILS

Section 1: Oil Composition

Oil samples were taken at wellhead from D-3 pools along the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller reef trends. For comparison, several oil pools in the Middle Devonian Keg River Formation at Zama were sampled. The oils were topped and analysed using the liquid chromatographic techniques discussed in Part 1, Chapter I of this thesis. Sulphur contents were determined on the untopped oils using the Parr Oxygen Bomb procedure outlined in Part 1, Chapter I. The sulphur percentages were not adjusted to topped oil values. Table II - III lists the raw average saturate, aromatic, maltene[+], NSO* and sulphur percentages for the pools sampled. The precision of these analyses is discussed in Part 1, Chapter I. A well by well summary of single and replicate analyses of crude oil compositions is presented in Appendix VII.

[+] Maltenes are the benzene soluble portion of the asphaltene fraction.

*The NSO fraction contains nitrogen, sulphur and oxygen compounds.

Table II - III

Oil Component Analyses Expressed as a Percentage of the Topped Oil

Pool - Field		Well Location	Saturates	Aromatics	Maltenes	NSO	Total	Sulphur[+]
Big Lake	D-3	13-25-53-26W4	46.2	33.2	2.5	9.6	91.5	0.38
		9-26-53-26W4	47.3	33.4	3.6	9.7	93.7	0.42
Acheson	D-3	4-10-52-26W4	59.3	27.4	2.3	5.7	94.7	0.14
Yekau Lake	D-3	8-4-52-26W4	57.9	25.8	2.4	6.2	92.3	0.13
Leduc Woodbend	D-3	13-3-50-26W4	58.4	27.0	2.6	6.0	94.0	0.29
		8-9-50-26W4	56.2	23.9	3.4	6.8	90.3	0.29
		8-5-51-26W4	56.0	24.8	2.6	6.7	90.1	0.30
Golden Spike	D-3	12-26-51-27W4	49.6	28.6	3.6	8.2	90.0	0.24
		10-27-51-27W4	50.8	29.1	3.7	7.7	91.3	0.24
Wizard Lake	D-3	1-21-48-27W4	53.0	26.4	3.5	7.6	90.5	0.21
Glen Park	D-3	4-2-49-27W4	55.1	28.6	3.1	6.3	93.1	0.19
		5-2-49-27W4	53.6	26.7	3.4	7.1	90.8	0.20
Bonnie Glen	D-3	14-6-47-27W4	62.4	25.3	1.9	3.9	93.5	0.21

[+] Sulphur abundances were calculated from the untopped oils.

TABLE II-III (Cont'd)

Pool - Field		Well Location	Saturates	Aromatics	Maltenes	NSO	Total	Sulphur⁺
Sylvan Lake	D-3	10-20-37-3W5	55.0	24.1	2.1	5.7	86.9	0.18
		10-17-37-3W5						
Westerose	D-3	4-3-46-28W4	62.7	23.2	1.6	4.0	91.5	0.30
West Drumheller	D-3	11-1-30-21W4	45.0	31.8	2.9	9.4	89.1	1.03
		12-1-30-21W4	45.8	32.7	2.9	9.4	90.8	0.95
New Norway		11-36-44-22W4	40.2	35.3	3.7	11.4	90.6	1.12
Buffalo Lake	D-3	4-35-39-21W4	28.3	43.1	4.3	11.7	87.4	2.44
Bashaw	D-3	10-6-42-22W4	53.1	26.7	2.1	6.1	88.0	0.81
Erskine	D-3	2-7-39-20W4	31.7	44.2	5.8	9.6	91.3	1.95
		6-19-39-20W4	30.5	43.1	5.4	11.3	90.3	1.81
		8-13-39-21W4	30.8	42.9	4.2	11.4	89.3	1.97
		8-26-39-21W4	29.9	42.9	5.1	13.0	90.9	1.79
Stettler	D-3	12-3-38-20W4	29.4	41.0	6.9	12.8	90.1	1.76
		16-9-38-20W4	29.9	41.6	4.4	11.8	87.7	1.83
		16-16-38-20W4	30.5	41.6	6.7	11.8	90.6	1.93
Malmo		5-14-44-22W4	48.4	30.3	3.0	8.7	90.4	0.50

⁺Sulphur abundances were calculated from the untopped oils.

TABLE II-III (Cont'd)

Pool - Field		Well Location	Saturates	Aromatics	Maltenes	NSO	Total	Sulphur⁺
Clive	D-3A	16-29-40-24W4	59.9	22.6	1.7	4.9	89.1	0.38
		12-33-40-24W4	55.3	23.4	1.8	4.7		0.33
Wimborne	D-3	6-11-33-26W4	55.7	27.5	1.3	4.8	89.3	0.96
		10-13-33-26W4	54.8	28.9	1.1	4.6	89.4	--
			- Keg River Oil Analyses -					
Zama Keg River		6-23-116-4W6	42.7	39.0	2.9	9.2	93.8	1.61
		12-21-117-4W6	45.0	38.0	3.7	7.3	94.0	1.03
		2-25-117-5W6	46.7	37.0	3.8	7.1	94.6	0.86
Virgo Keg River		5-27-114-5W6	48.4	32.0	1.8	5.9	88.1	0.87
		5-11-115-5W6	48.0*	32.1	2.1	4.7	86.9	0.75

⁺Sulphur abundances were calculated from the untopped oils.
*Adjusted value.

The objective of the oil analysis was not to classify the oils according to their chromatographic fraction abundances but to provide crude oil fractions whose carbon isotope abundance could be determined and to isolate the saturate fraction so that the extent of biodegradation of the oil pool could be assessed. However, a Q-mode factor analysis of the chromatographic fraction data and the oil sulphur contents has provided considerable insight into oil origin and alteration histories. Before discussing the results of this factor analysis it is necessary to comment on the problem of data interpretation in closed number systems.

a) Closed Number Systems

When quantities are normalized[+], any significant increase in the abundance of one component of a system will result in a decrease in the normalized abundances of the other components even though their values prior to normalization may not have changed. This type of spurious negative correlation between normalized variables has been produced by the requirements of the closed system and has been discussed by Chayes

---

[+] Here the normalization procedure refers to the mathematical transformation of abundances to a constant sum which is usually 1 or 100. Such systems are said to be closed.

(1960, 1962, 1970). Therefore, relationships determined between variables in closed number systems, whether observed by scatter diagrams, correlation coefficients or other means, may not be genuine, but produced by the constraints of the constant sum. As noted by Miesch (1976) it is difficult or impossible to decide what part is spurious. A qualitative test that determines if changes in the abundance of a particular variable in a closed number system are natural or artifical is developed in the following discussion.

Consider a system consisting of n variables whose measured abundances are A, B, C, D, ... n. Two samples in the system are defined by the abundances:

Sample 1: $A_1, B_1, C_1 \ldots n_1$

Sample 2: $A_2, B_2, C_2 \ldots n_2$

The normalized abundances in Sample 1 are defined as:

$$N_{A1} = \frac{A_1}{A_1 + B_1 + C_1 + \ldots + n_1}$$

$$N_{B1} = \frac{B_1}{A_1 + B_1 + C_1 + \ldots + n_1}$$

$$N_{n1} = \frac{n_1}{A_1 + B_1 + C_1 + \ldots + n_1}$$

Where $N_{A1} + N_{B1} + N_{C1} + \ldots + N_{n1} = 1.0$

In a similar way the normalized abundances for sample 2 can be defined. Also for sample 2:

$$N_{A2} + N_{B2} + N_{C2} + ... + N_{n2} = 1.0$$

If the abundances of the variables in sample 1 and sample 2 have the following relationships:

$$A_1 > A_2;\ B_1 = B_2;\ C_1 = C_2;\ ....;\ n_1 = n_2$$

then the inequalities:

$$N_{B1} < N_{B2};\ N_{C1} < N_{C2};\ ....\ N_{n1} < N_{n2}$$

are artificial, having been produced by the normalization calculation.

$$\text{Let } \frac{A_1 + B_1 + C_1 + ... + n_1}{A_2 + B_2 + C_1 + ... + n_2} = \frac{1}{M} \qquad \text{II - 3}$$

where M is the fraction that system 2 is smaller than system 1.

$$\text{Since } N_{A1} = \frac{A_1}{A_1 + B_1 + C_1 + ... + n_1} \text{ and, } N_{A2} = \frac{A_2}{A_2 + B_2 + C_2 + ... + n_2}$$

$$\text{then } \frac{N_{A1}}{N_{A2}} = \frac{M.A_1}{A_2}. \qquad \text{II - 4}$$

$$\text{Also, } \frac{N_{B1}}{N_{B2}} = M;\ \frac{N_{C1}}{N_{C2}} = M;\ ....;\ \frac{N_{n1}}{N_{n2}} = M \qquad \text{II - 5}$$

In the case where the abundance of more than one variable in sample 1 changes, equation II - 5 must be modified to exclude the changed variables and equation II - 4 must be rewritten. If both A_1 and B_1 vary then:

$$\frac{A_1 + B_1}{A_2 + B_2} = \frac{N_{A1} + N_{B1}}{N_{A2} + N_{B2}} \times \frac{1}{M'} \qquad \text{II - 6}$$

Using equations II - 4 to II - 6 the artificial variation of any component in a closed system can be qualitatively assessed. For example, consider the normalized abundances in Table II - IV. Sample 1 is described by the average normalized abundances of the saturate, aromatic, maltene and sulphur components from the Westerose oil. Sample 2 is defined by these four components from the Big Lake oil. These two oils represent samples from a high temperature and low temperature pool, respectively, along the Homeglen-Rimbey-Redwater D-3 reef trend. The saturate content of the Westerose Oil is markedly higher than the saturate content of the Big Lake oil, while the aromatic, maltene and sulphur contents in the Westerose oil are much lower. It is possible that the normalized abundances of the Westerose

TABLE II - IV

Normalized Average Oil Compositions for D-3 Pools

Pool	Saturate %	Aromatic %	Maltene %	Sulphur %	Reservoir Temp °C
Westerose D-3	71.5	26.4	1.8	0.3	82°C
Big Lake D-3	56.0	39.9	3.6	0.5	58°C
Buffalo Lake D-3	36.2	55.5	5.5	3.1	57°C
Wizard Lake D-3	64.2	31.5	4.1	0.2	72°C

oil fractions were produced by increasing only the saturate content of the Big Lake oil through a process such as thermal maturation. Let the normalized abundances of the saturates, aromatics, maltenes and sulphur be N_A, N_B N_C and N_D. Then, by using equation II - 5 the M values for these four variables from the Big Lake oil (sample 2 equivalent) and Westerose oil (sample 1 equivalent) were calculated and listed in Table II - V. From these M values, A_1/A_2 ratios were determined from equation II - 4 using the calcualted N_{A1}/N_{A2} ratio of 1.28. When the precision of the aromatic, maltene and sulphur analyses is considered

TABLE II - V

Closed System Factors Calculated from the Composition of the Big Lake and Westerose Oils.

Component	M	A_1/A_2	
Aromatics	0.662	1.93	N_{A1}/N_{A2} = 1.28
Maltenes	0.500	2.56	
Sulphur	0.600	2.13	

(SD.M = 0.05 to 0.20; see Part I, Chapter II) the difference in the M ratios in Table II - V is not significant. Consequently the variation in the normalized aromatic, maltene and sulphur abundances between the

Big Lake and Westerose oils may only be the result of the constraints of the closed number system, and not genuine. The saturate content of the Big Lake oil need only be increased by a factor of around 2.2 to produce the observed changes in the abundance of the other three compounds. If a similar comparison is made between the low sulphur Big Lake oil and the high sulphur Buffalo Lake oil (refer to Table II - IV and Table II - VI the disparity between the saturate, aromatic and maltene contents can also be explained by the closed number system. The saturate content of the Big Lake oil need only be reduced by a factor of about 2.3 to cause the observed changes, within the error of analysis, in the normalized aromatic and maltene contents of the Buffalo Lake oil. On the other hand, such a large disparity in the normalized abundance of the sulphur variable in these oils cannot be

TABLE II - VI

Closed System Factors Calculated from the Composition of the Big Lake and Buffalo Lake Oils.

Component	M	A_1/A_2
Aromatics	0.723	2.14
Maltenes	0.654	2.37
Sulphur	0.161	9.60

$N_{A1}/N_{A2} = 1.55$

explained by the constraints of the constant sum. The Buffalo Lake oil may therefore have received a natural increment in its sulphur content.

Not all of the oil pair comparisons show such a high degree of dependence on the closed system effect. The comparison between the normalized abundances of the saturate, aromatic, maltene and sulphur components in the Big Lake and Wizard Lake oils is an example. Not one of the M factors listed in Table II - VII is similar within a reasonable value of analytical precision. In this case, as noted by Miesch (1976), the amount of variability in the data accounted for by the closed number system is uncertain.

TABLE II - VII

Closed System Factors Calculated from the Composition of the Big Lake and Wizard Lake Oils.

Component	M	A_1/A_2	
Aromatics	0.790	1.45	$N_{A1}/N_{A2} = 1.15$
Maltenes	1.140	1.00	
Sulphur	0.400	2.86	

In the above comparisons between the Big Lake and Westerose oils and the Big Lake and Buffalo Lake oils, a variation in the saturate content by a factor of around 2X was required to produce the observed variation in the normalized abundances of the other variables. If variations in the saturate content of such a magnitude are possible, then the hypothesis that much of the variability in the data is caused by the closed number system effect, together with the analytical precision, cannot be rejected. This implies, but does not prove, that there may be no natural variability in the components whose M values are equal. If a factor of 2 is not a reasonable value, then there is a degree of genuine variability in the components with equal M values, though the amount of this variability is uncertain.

These oil pair comparisons point out that the variability of the oil fraction data could be controlled almost completely by the variability of one or two components (saturates and sulphur) through the closed number system effect. Consequently inferences of the role of processes such as maturation, biodegradation, sulphurization and deasphalting based on correlations amongst oil fraction data are of uncertain value.

b) Q-Mode Factor Analysis of the Oil Fraction Data

Q-Mode factor analysis (refer to Joreskog _et_ _al_. 1976) is a multivariate technique that is not greatly affected by the closed number system problem (Miesch, 1976) and, therefore, is well suited to the interpretation of constant sum chemical analyses. This method classifies objects (samples) in terms of fundamental characteristics (factors) which have been derived from measurements of variables which characterize the object. However, the processes (geochemical) which are responsible for the classification cannot necessarily be directly inferred from the Q-mode analysis.

A data matrix consisting of 5 oil composition variables and 51 oil samples was constructed for Q-mode factor analysis (see Table II - III). The 5 composition variables were the contents of saturates, aromatics, maltenes, NSO's and total sulphur in the oil samples. The 47 oils consisted of single pool samples, duplicate and triplicate samples from a single well sample and samples taken from more than one well in the same pool. Oil samples were taken from Upper Devonian D-3 pools along the Wimborne-Duhamel, Homeglen-Rimbey-Redwater and Stettler-West Drumheller reef trends. For comparison, a fourth suite of oil samples was taken from the Middle Devonian Keg River pools at the Zama-Virgo field in N.W. Alberta. From what is known about the D-3 Formation hydrodynamics (Hitchon, 1969, 1969b and 1971) and the closely related phenomenon of oil migration, and from a study of oil-source rock correlations (Deroo et al. 1977) it is very likely that the Leduc oils have had a common source. The marked differences in the D-3 oil compositions noted by Hitchon (1964) and observed in this study (see

Table II - III) can therefore be attributed to alteration factors that affected these oils during generation, primary migration, secondary migration, or during their period of residence in the reservoir trap. It has been assumed that the oil source does not have a large inherent variability. By including the Keg River oils, a suite of samples whose source was probably different from the D-3 oils was introduced to the data matrix. It was expected that the Q-mode analysis would define a source factor, and one or two factors related to oil metamorphosis by processes such as maturation, biodegradation, deasphalting (refer to Evans et al. 1971) and sulphurization (refer to Pryor, 1962).

The technique used in the Q-mode factor analysis to define the symmetrical similarity matrix, H, from the percentage range scaled row normalized data matrix, W (refer to Joreskog et al. 1976) was the cosine theta index described by Imbrie and Purdy (1962). This index emphasizes proportions and not magnitudes. The cosine theta index is suited to the measurement of similarities between the row vectors of the W matrix when the variables (columns) represent chemical compositions. Q-mode analysis classifies samples according to their similarities with reference to a minimum number of extracted factors. The Q-mode program used was CABFAC which has been described by Klovan and Imbrie, 1971.

In Table II - VIII the eigenvalues for the principle components solution are listed. Figure II - 3 illustrates a plot of normalized varimax factor components for three factors extracted from the scaled

TABLE II - VIII

Eigen Values

No.	Eigenvalue	Cum. Variance
1	35.8469	76.27
2	9.3131	96.09
3	1.1635	98.56
4	0.3742	99.36

percentage range row normalized matrix of oil samples and compositions. The communalities for the three factor varimax factor component matrix (refer to Table II - IX) were all in excess of 92% and generally in excess of 97%. The communality is a gauge of the ability of the chosen x factors, here 3, to reproduce, in x factor space, the position of the scaled row normalized object, represented in n variable space, where x is usually less than n. The larger the communality, the more exactly is the original object described by the factors. In Figure II - 3 the oil samples plot as a continuum between Factor I and Factor II, with

FIGURE II-3
PLOT OF THE NORMALIZED VARIMAX FACTOR COMPONENTS FOR THREE FACTORS

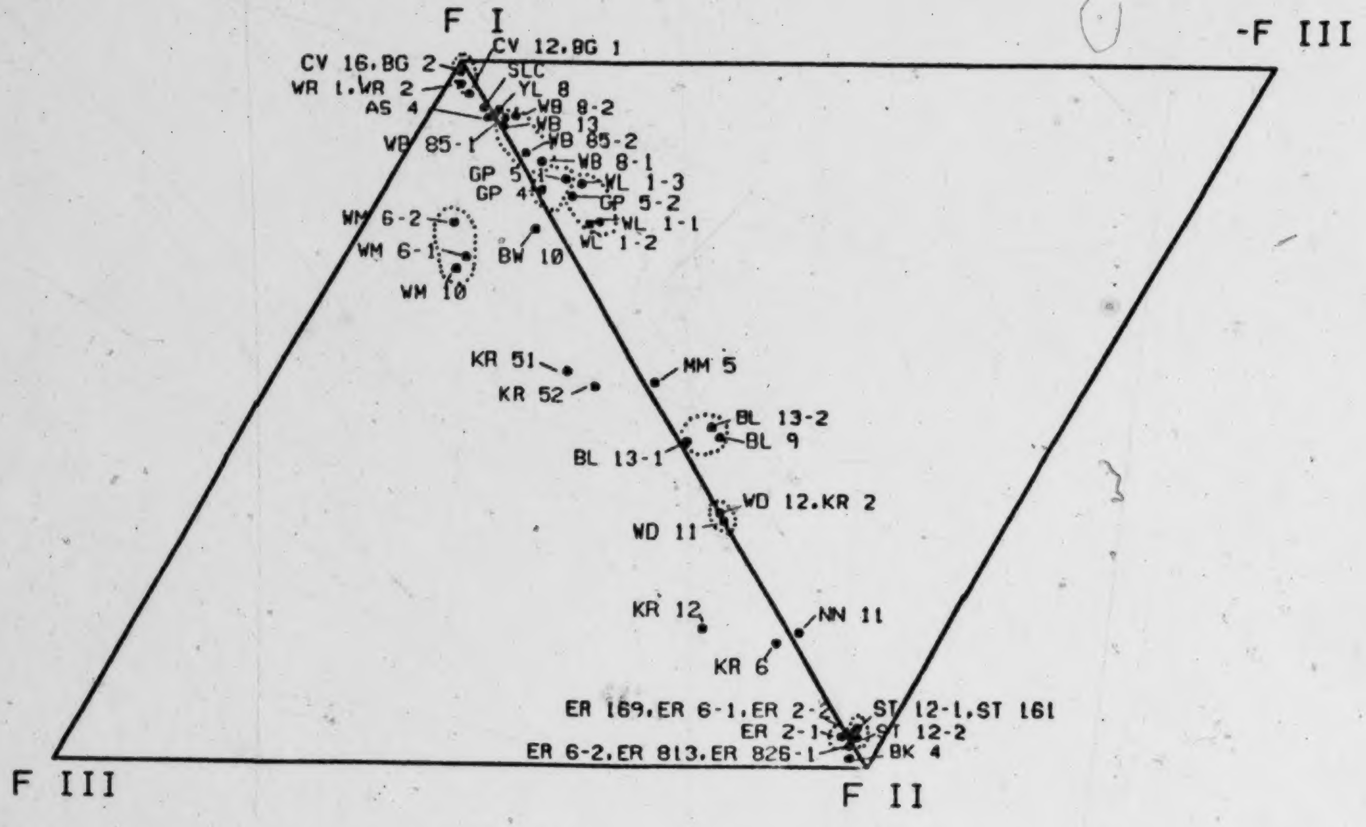


TABLE II - IX

Varimax Factor Matrix for Three Factors

Well	Comm.	I	II	III
BL 13-1	.9161	.6470	.7006	-.0810
BL 13-2	.9531	.6523	.7132	-.1380
BL 9	.9834	.6564	.7221	-.1767
AS 4	.9897	.9624	.2505	.0262
YL 8	.9984	.9657	.2537	-.0387
WB 8-1	.9723	.9038	.3655	-.1477
WB 8-2	.9793	.9424	.2835	-.1037
WB 85-1	.9941	.9597	.2680	-.0357
WB 85-2	.9929	.9254	.3626	-.0719
WB 13	.9981	.9490	.3115	.0218
GS 12-1	.9934	.7867	.5670	-.2305
GS 12-2	.9907	.7885	.5729	-.2017
GS 10	.9946	.8083	.5534	-.1872
WL 1-1	.9993	.8648	.4716	-.1703
WL 1-2	.9854	.8493	.4622	-.2245
WL 1-3	.9955	.8826	.4205	-.1989
BG 1	.9737	.9618	.0370	.2173
BG 2	.9993	.9891	.0956	.1085
SLC	.9988	.9772	.2089	-.0165
WR 1	.9946	.9811	-.0160	.1780
WR 2	.9960	.9795	.0526	.1837
WD 12	.9830	.5914	.7950	.0351
WD 11	.9781	.5853	.7969	.0210
NN 11	.9823	.4305	.8894	-.0776
BL 4	.9910	.1151	.9789	.1399
BW 10	.9851	.8596	.4576	.1918
ER 2-1	.9625	.1930	.9578	.0886
ER 2-2	.9873	.1833	.9754	.0467
ER 6-1	.9917	.1942	.9764	.0239
ER 6-2	.9998	.1657	.9859	.0189
ER 813	.9982	.1762	.9805	.0753
ER 826-1	.9957	.1777	.9818	-.0131
ER 826-2	.9983	.1780	.9829	-.0228
ST 12-1	.9773	.1988	.9596	-.1298
ST 12-2	.9904	.1778	.9735	-.1054
ST 169	.9969	.1717	.9833	.0255
ST 161	.9823	.1991	.9678	-.0767
MM 5	.9910	.7323	.6675	-.0959
CV 12	.9946	.9786	.1473	.1236
CV 16	.9914	.9836	.0903	.1255
WM 6-1	.9980	.8288	.3807	.4076
WM 6-2	.9646	.8484	.3136	.3826

TABLE II - IX (Cont'd)

Well	Comm.	I	II	III
KR 12	.9720	.5285	.8236	.1202
KR 6	.9948	.4132	.8832	.2098
KR 2	.9633	.5890	.7810	.0795
KR 51	.9911	.7118	.6315	.2926
KR 52	.9695	.7301	.5839	.3090
GP 4	.9855	.9042	.4045	-.0650
GP 5-1	.9869	.8764	.4395	-.1600
GP 5-2	.9992	.8960	.4128	-.1612
WM 10	.9979	.8163	.3753	.4368
Variance		53.332	42.484	2.808
Cum. Var.		53.332	95.816	98.624

a slight tendency to plot in Factor III space. Since replicate analyses of oil samples and analyses of more than one well from a pool have been included in the data matrix, approximate confidence areas can be defined. These are represented by dashed ellipsoids in Figure II - 3. Oil samples that lie within an ellipsoid cannot, with any confidence, be said to be from different pools. Considering the single pool and analytical variability, only the Wimborne oils, possibly the Bashaw oil and all but two Keg River oils plot off the Factor I - Factor II join in the positive Factor III quadrant. Within the limits of single pool data variability, Wizard Lake, Glen Park, Golden Spike and Big Lake oils plot off of the Factor I - Factor II join in the negative Factor III quadrant. The remaining oils plot along the Factor I - Factor II join.

c) Interpretation of the Q-Mode Factors

An interpretation of the three factors extracted from the D-3 oil fraction data is essentially a definition of the alteration processes that have affected the oils and a definition of the oils' source. The interpretation of the factors is facilitated through the factor scores matrix (see Table II - X). According to Joreskog *et al*. (1976) the varimax factor loading matrix, A, can be computed from the product of the scaled percentage range row normalized data matrix, W, and the varimax factor scores matrix, F. That is: $A = WF$ (II - 7) Also, $W = AF'$ (II - 8) where F' is the transpose of the F matrix. Therefore the position of the original row normalized object in n variable space can be referenced exactly in x factor space when the communalities are equal to unity, that is when all of the factors are used. When the communalities are less than unity, that is when only a few of the extracted factors are used, the following relationship applies: $\hat{W} = \overset{*}{A}\overset{*}{F}$ (II - 9). $\hat{W}$ is a matrix which approximates the exact W matrix and $\overset{*}{A}$ is a matrix of rotated factor loadings which correspond to the reduced matrix of factor scores, $\overset{*}{F}$. The larger the communality of the matrix of factor loadings, the better is the approximation of the W matrix by the matrix, $\hat{W}$. The factor reduced equivalent to equation II - 7 is: $\hat{A} = W\overset{*}{F}$ (II - 9). It is this equation that can be used to interpret the meaning of the factors from the factor scores matrix. Equation (II - 9) states that the varimax factor loadings for x factors, here x is 3, can be calculated by the matrix multiplication of the scaled percentage range row normalized data matrix for n variables, W, by the reduced factor scores matrix, $\overset{*}{F}$.

Referring to the $\overset{*}{F}$ matrix for 3 factors, in Table II - X, it is apparent that the position of the 5 variable oil sample in 3 factor space, with reference to the first factor, is controlled mainly by the saturate factor score. The maltenes and NSO's have only a minor input to the Factor I loading and the sulphur and aromatic contents have an even smaller contribution. In Figure II - 4 the varimax Factor I loadings have been plotted versus present day reservoir temperature. Three oil groups can be defined based on relative data grouping and

FIGURE II - 4

PLOT OF VARIMAX FACTOR I LOADINGS vs. FORMATION TEMPERATURE

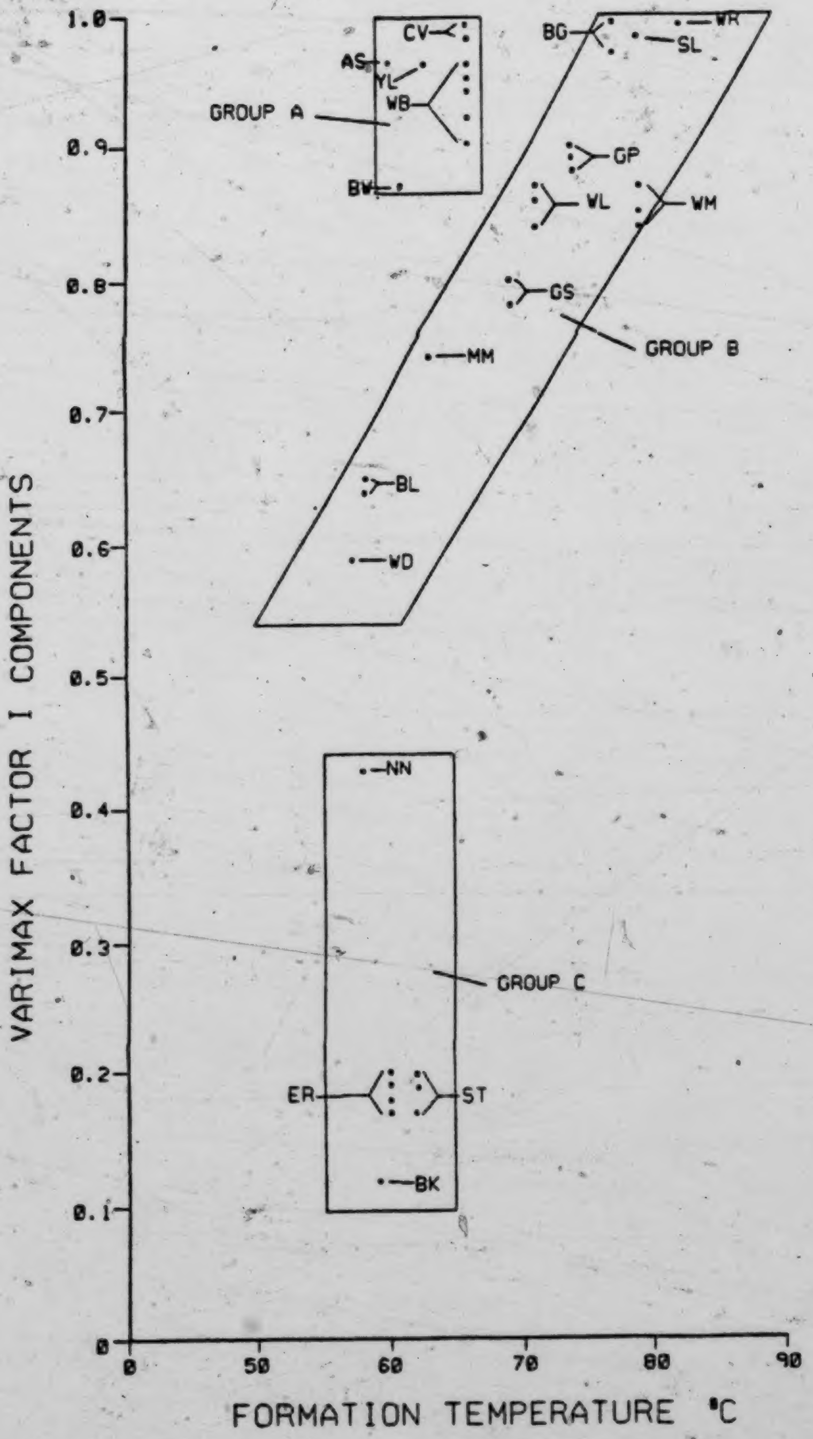


TABLE II - X

Varimax Factor Scores Matrix

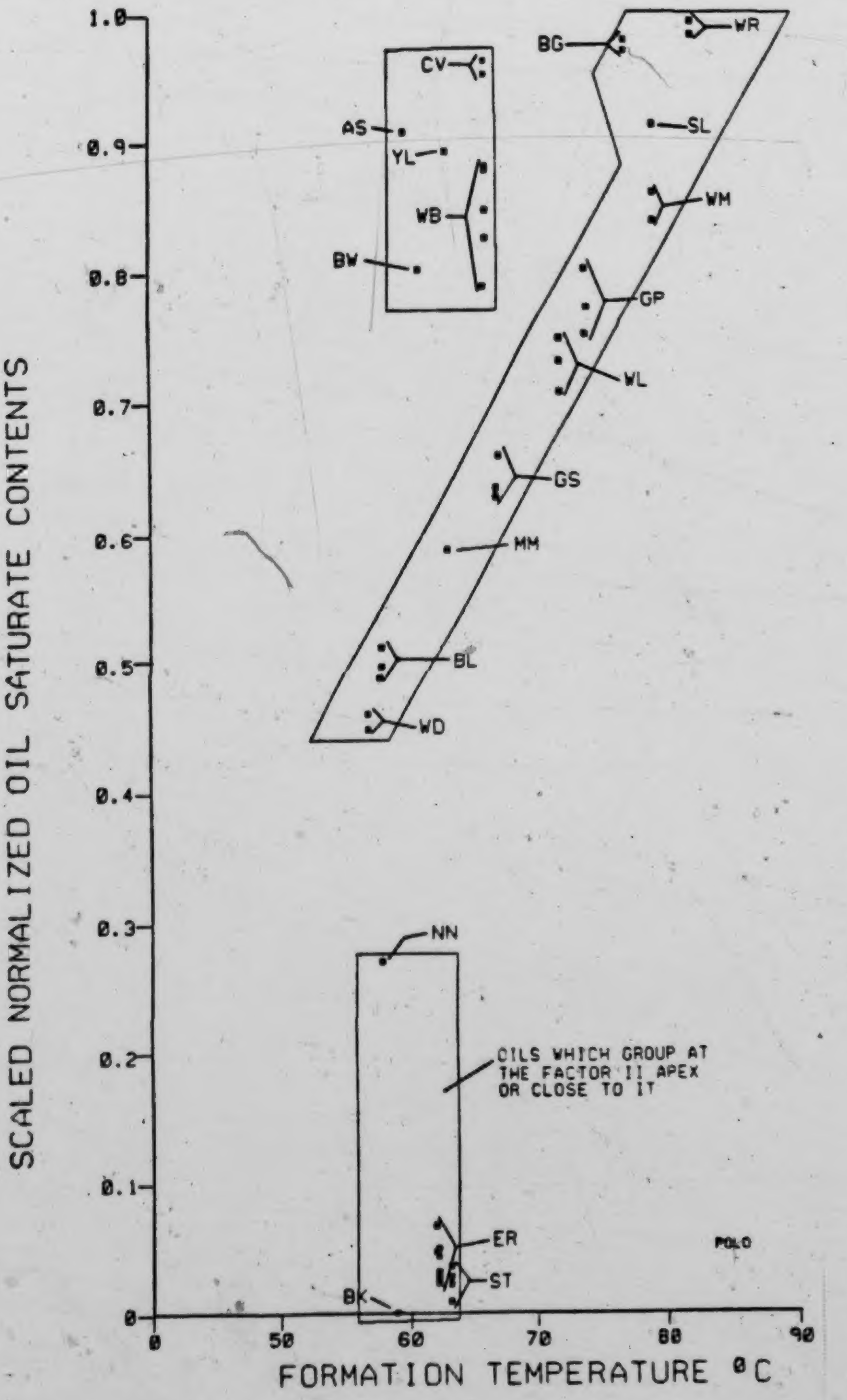
	Factor Scores		
Variable	I	II	III
Saturates	0.974	-0.144	0.175
Aromatics	0.026	0.593	0.271
Maltenes	0.138	0.379	-0.437
NSOs	0.174	0.517	-0.529
Sulphur	-0.038	0.466	0.652

have been designated as: Group A, Group B and Group C. On the basis of other parameters such as n-C_{16}/n-C_{31} ratios and sulphur and carbon isotope data, the West Drumheller oil will be classed with Group C oils. Group B oils have a statistically significant positive linear correlation between Factor I values and present day reservoir temperature [for a sample (N) of 13, the correlation coefficient (r) is 0.95] which suggests that Factor I reflects the maturation process. Little confidence can be placed in the apparent negative correlation between Group C Factor I values and present day reservoir temperature. The Group C sample size (5 oil pools) is too small, and the variability in the data too low to do a meaningful statistical analysis. Group A oils have a large varimax Factor I component but have no correlation of this component with reservoir temperature. The fact that these oils would have to be shifted to higher reservoir temperatures to plot with Group B is interesting. If Factor I does represent the maturation process, then the Group A oils have matured at reservoir temperatures greater than their present values. Group A oils might have been affected by geothermal anomalies (hot spots) that have since subsided. An analysis of the state of maturation of the kerogen in the shales capping the Group A reservoirs could support or negate this contention. An equally possible and preferable explanation is that the Group A oils are up dip accumulations of oil which has been displaced from deeper, hotter, D-3 traps by gas. Gussow (1954) convincingly argued that this spill point migration process occurred in the D-3-Cooking Lake reservoir along the Homeglen-Rimbey-Redwater trend. Figure II -5 is a plot of the scaled percentage range row normalized+ saturate contents versus present day reservoir temperature for the D-3 oils. The same 3 oil groups are defined, but the correlation of the saturate content with reservoir temperature for the Group B oils is much better than the correlation of the varimax Factor I component with present day reservoir temperature.

+The percent range row normalization scaling calculation is an option in the Q-mode factor analysis programme, CABFAC (Klovan and Imbrie, 1971). This procedure has been discussed by Miesch (1976).

FIGURE II-5

PLOT OF THE SCALED NORMALIZED OIL SATURATE CONTENT vs FORMATION TEMPERATURE



If Factor I does represent the maturation process, plotting the Factor I varimax components against a maturation parameter defined from the composition of the oils should result in a significant positive correlation and Group A oils should be incorporated into Group B. Group C oils should remain a distinct group since their compositions are controlled almost entirely by Factor II. The maturation parameter defined for this plot (see Figure II - 6) was the $n\text{-}C_{16}/n\text{-}C_{31}$ ratio for normal paraffins isolated from the saturate fraction using an OV 101 column (refer to Part I, Chapter I). The $n\text{-}C_{16}$ and $n\text{-}C_{31}$ peak heights above the napthenic envelop of the chromatogram were measured and the ratios calculated. The variability in the data due to analytical error and pool inhomogeneities is reflected by the spread of the replicate data points for the Erskine, Stettler, Big Lake, Glen Park, Wizard Lake and Woodbend pools (see Figure II - 6). Maturation affects the n-paraffin homologs by decreasing their chain length, that is, cracking the alkane molecules (McNab _et_ _al_. 1952; Morrison and Boyd, 1968). As a result the $n\text{-}C_{16}/n\text{-}C_{31}$ ratio will increase with increasing intensity of maturation or with increasing length of exposure to a certain level of maturation. In the reservoir, oil is matured in a time-temperature framework and the $n\text{-}C_{16}/n\text{-}C_{31}$ ratio will be controlled by both temperature and length of exposure of the oil to a specific temperature or temperature gradient (Connan, 1974). In Figure II - 6 the $n\text{-}C_{16}/n\text{-}C_{31}$ ratio has been plotted versus the varimax component for Factor I. Group A oils have merged with Group B and the combined

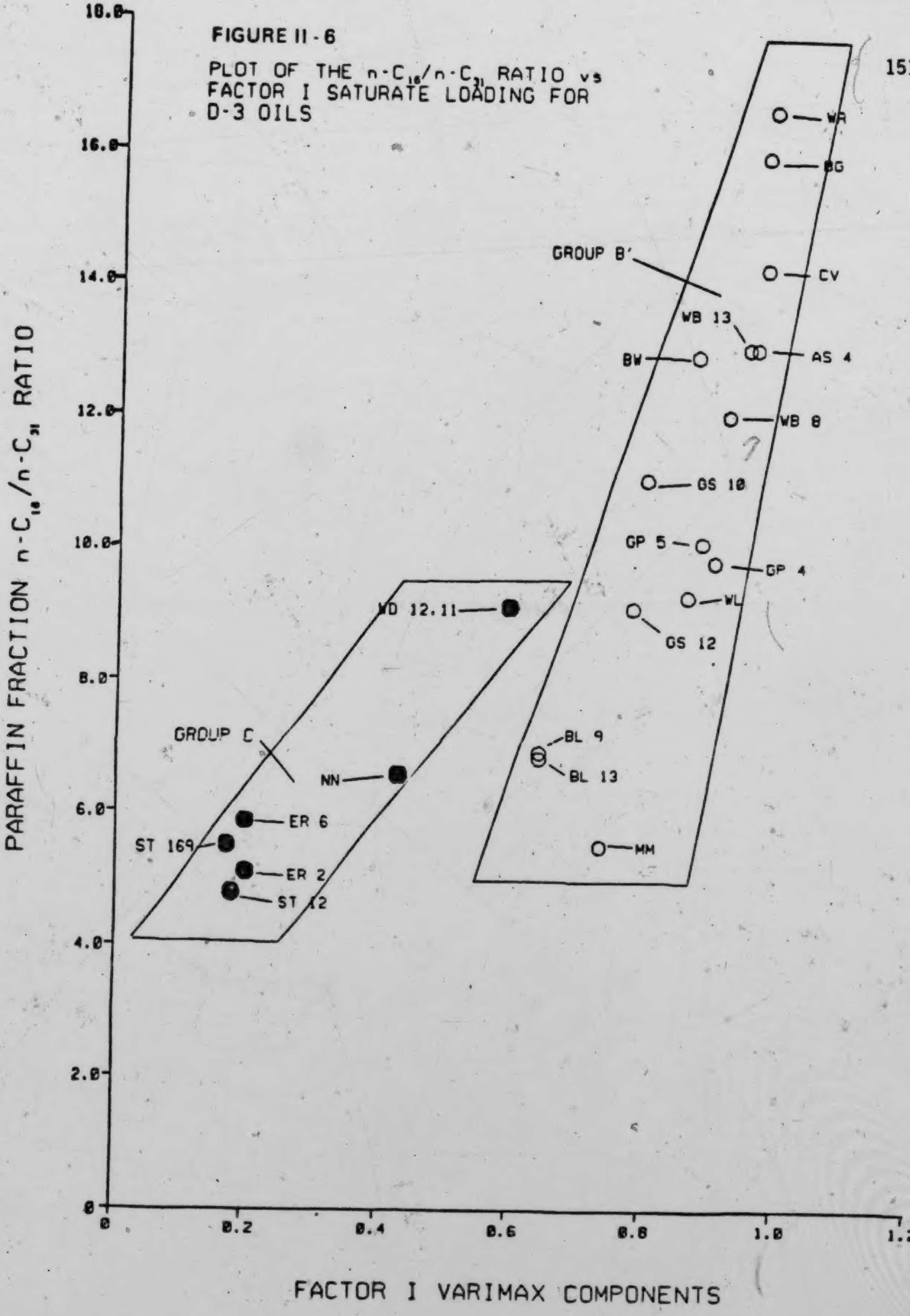


FIGURE II-6

PLOT OF THE $n\text{-}C_{18}/n\text{-}C_{31}$ RATIO vs FACTOR I SATURATE LOADING FOR D-3 OILS group (Group B') shows a statistically significant positive correlation with temperature. Group C oils remain a distinct group, and the West Drumheller oil has been included with this group.

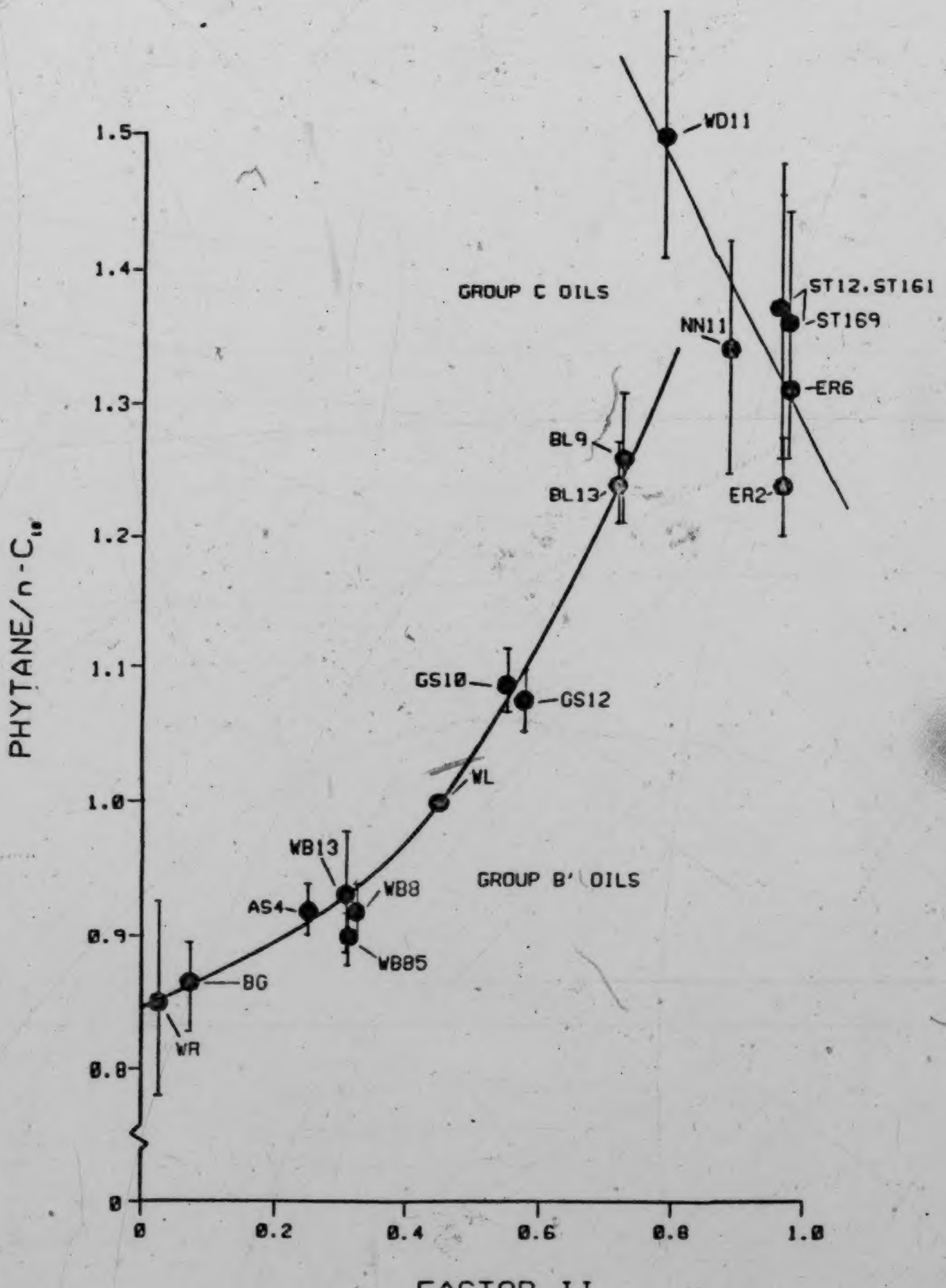
The factor scores for Factor II (see Table II - X) show that the loading of oil compositions onto the second factor is controlled almost equally by the aromatic, NSO, total sulphur and maltene variables. The saturate factor score produces only a minor negative loading of the saturate contents onto Factor II. Published data by Toland (1960), Pryor (1962), Bestougeff and Combaz (1973) and Gousseva and Faingerch (1973) indicate that Factor II may reflect the sulphurization process of a crude oil and the related hydrogen sulphide generation reaction within the reservoir trap. These authors provide experimental evidence that shows the sulphurization of a crude oil results in an increase in its sulphur content as well as increases in its aromatic, NSO and asphaltene abundances (refer to Part II, Chapter I). These same four oil fractions are emphasized by the Factor II scores. The Stettler, Erskine and Buffalo Lake oils which have the highest Factor II values, also have the highest oil sulphur contents and the highest volume percentage of hydrogen sulphide in their solution gases (see Table II - II). This is consistent with the oil sulphurization reactions discussed by Toland (1960) and Pryor (1962).

A satisfactory interpretation of the third factor cannot be given. The largest factor scores for Factor III (refer to Table II - X) are the maltene and NSO values (negative) and the sulphur value (positive). Consequently, Factor III may be related to the deasphalting (see Evans et al. 1971) and the sulphurization processes. Three of the five Keg River oils plot in the positive Factor III quadrant which suggests that Factor III may in part represent oil source. However, the D-3 Wimborne samples also plot in the positive Factor III quadrant, and two Keg River oils plot along the Factor I - Factor II join. Either the Keg River and D-3 oils have a very similar source or the oil fraction abundances cannot be used to discriminate between oils from different sources.

Because the oil composition matrix reduces to essentially a two factor system, the varimax factor loadings matrix is closed. As a result Factor I and Factor II have a built in negative correlation which is unrelated to natural variations in the oils' compositions. The plot of the oil samples as a continuum between Factor I and Factor II in Figure II - 3 is a direct result of this closure. Furthermore the correlation between Factor I and parameters such as reservoir temperature, n-C_{16}/n-C_{31} ratio, etc. could be made, but in a negative sense, using Factor II (see Figure II - 7). However, these Factor I or Factor II plots define separate oil groups which do not form opposite ends of a continuous trend. Furthermore, the interpretation of the factors in

FIGURE II-7

PLOT OF THE PHYTANE/n-C_{18} RATIO vs FACTOR II CONTENT OF D-3 OILS (COMPARE WITH FIGURE II-9)



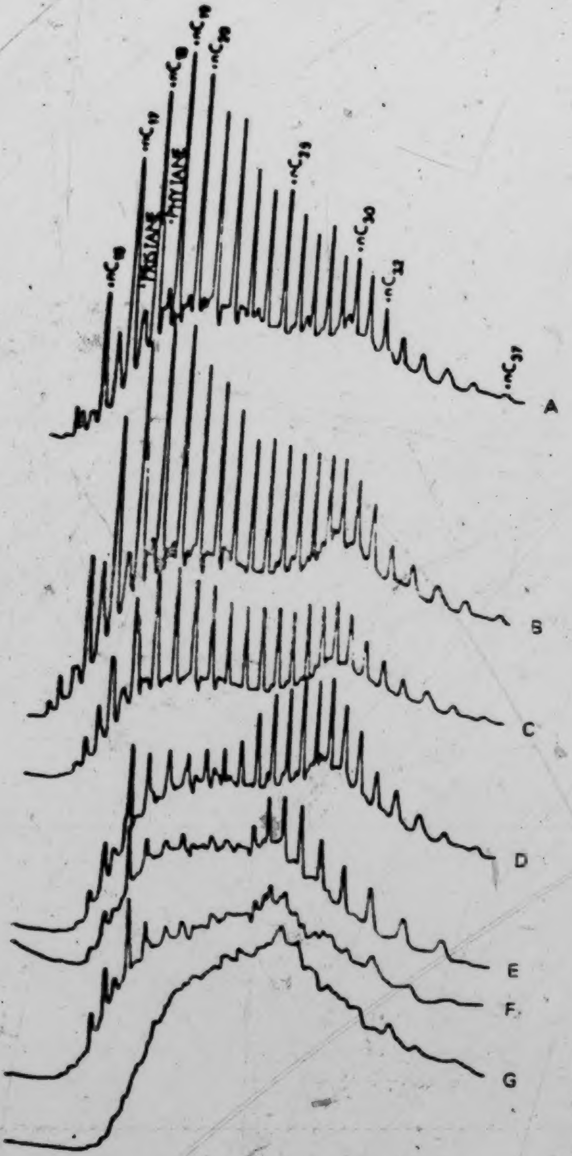
terms of the factor scores is still valid in spite of the closure of the factor loadings matrix. Therefore, the interpretation of Factor I and Factor II as a reflection of the maturation and sulphurization processes, respectively, is still valid.

d) Biodegradation of D-3 and Keg River Oils

The bacterial alteration of the D-3 and Keg River oils cannot be excluded as a process which has affected the composition of these oils on the basis of the above factor analysis. Biodegradation through a closed number system effect, increases the contents of aromatics, asphaltenes and sulphur in an oil at the expense mainly of the n-paraffins which are preferentially metabolised by the bacteria (Jobson _et_ _al_. 1972). To some extent, asphaltenes are generated during biodegradation (Bailey _et_ _al_. 1973). Sulphur can also be produced, as hydrogen sulphide, by the symbiotic association of the anaerobic sulphate reducing bacteria with the aerobic oil degrading bacteria. Therefore Factor II with its near equal emphasis on the aromatic, asphaltene, NSO and sulphur components could also reflect biodegradation. Furthermore, the nearly complete control of Factor I by the saturate oil component could be argued as a case for the bacterial alteration process since the n-paraffin portion of the saturates is preferentially utilized by the bacteria.

There are other variables which make unacceptable the interpretation of Factor I and Factor II as a reflection of biodegradation. Figure II - 8 illustrate a comparison of n-paraffin profiles for oils which have decreasing Factor I contents and for oils which have undergone progressively greater degrees of biodegradation. The abundant C_{13} to C_{20} n-paraffin peaks, the relatively low C_{30}^{+} n-paraffin contents and the relatively broad-low napthenic base regardless of the Factor I value for the D-3 oils are in marked contrast with the biodegraded oils. The degraded oil profiles (reproduced from Jobson et al. 1972) show increasingly depleted n-C_{13} to n-C_{20} contents, increasing contents of C_{30}^{+} n-paraffins and a shortening and peaking of the napthenic envelop as the extent of bacterial alteration intensifies. No oil for which a saturate profile was run for this thesis, including the Keg River oils, showed conclusive evidence of biodegradation. Phytane, an isoprenoid, is an organic fossil (Barghoorn et al. 1965 and Eglington and Murphy, 1969) produced directly from one of the more complex biological molecules. It is not a product of the multistep petroleum maturation reactions. Its branched structure gives phytane a resistance to bacterial consumption and as a result the peak height of phytane grows relative to n-C_{18} as the oil becomes progressively more biodegraded. Therefore a plot of the Phytane/n-C_{18} ratio for bacterially altered oils should show significant trends. In Figure II - 9 the Phytane/n-C_{18} ratio has been plotted versus the varimax Factor I component. The correlations defined are statistically significant. The same two oil groups defined by the n-C_{16}/n-C_{31} vs. Factor I plot (see

FIGURE II - 8



Gas-liquid chromatographic analyses of residual saturate fractions from sequential utilization of oil by mixed population at 30 C (A) Saturate fraction of control North Cantal Oil. (B) Residual saturates after 2 days of incubation. (C) Residual saturates after 3 days of incubation. (D) Residual saturates after 4 days of incubation. (E) Residual saturates after 5 days of incubation. (F) Residual saturates after 14 days of incubation. (G) Residual saturates after 21 days of incubation. (From Jobson et al, 1972)

N - ALKANE DISTRIBUTION IN "TOPPED" LEDUC AND KEG RIVER OILS

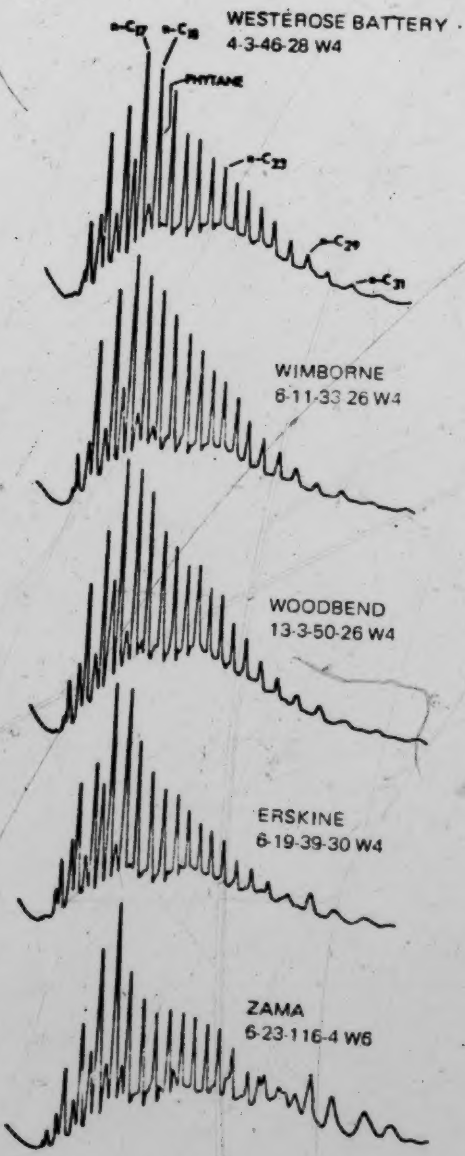


FIGURE II-9
PLOT OF THE PHYTANE/n-C_{18} RATIO vs FACTOR I CONTENT OF D-3 OILS

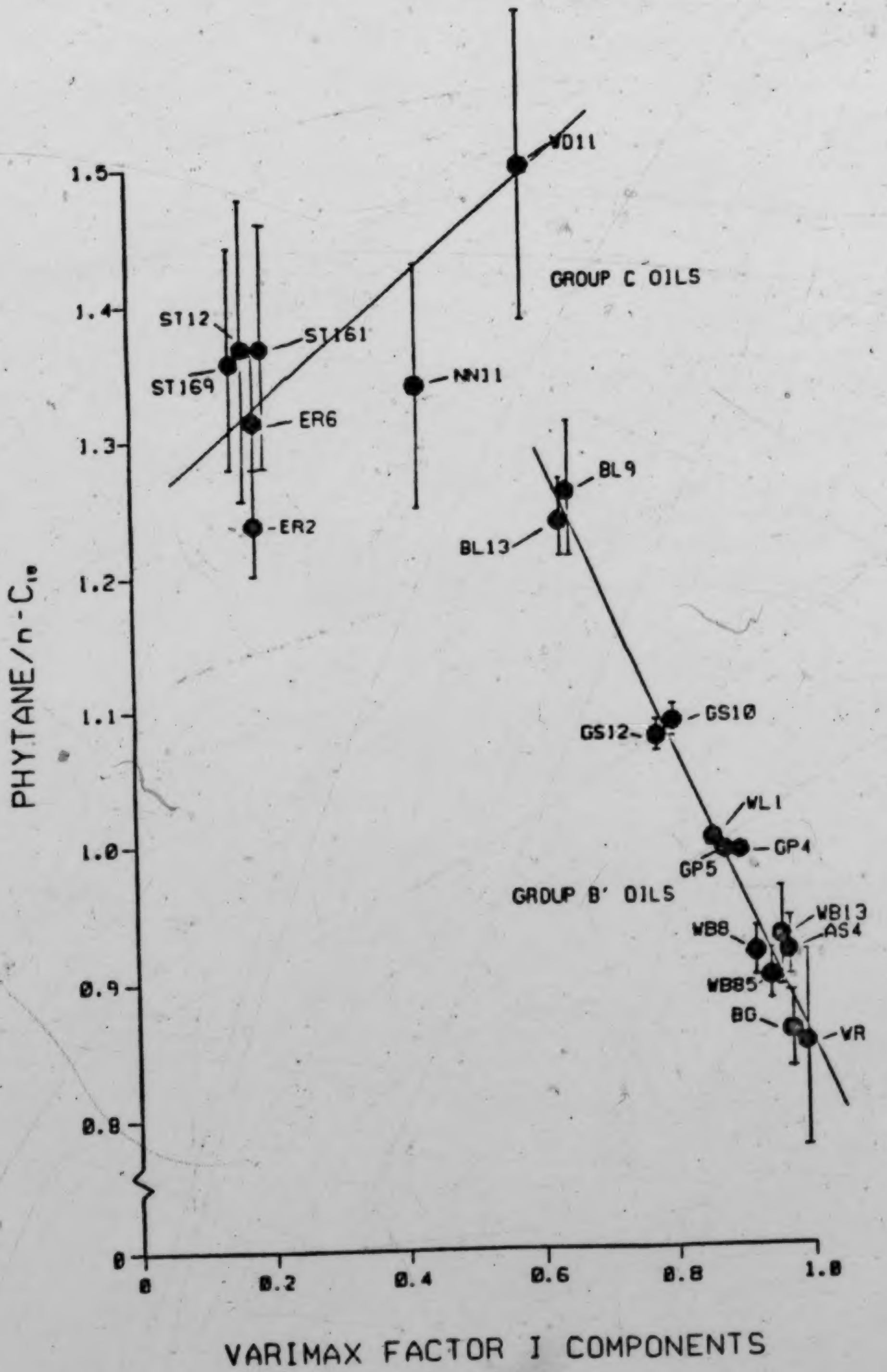


Figure II - 6) are defined in the Pytane/n-C_{18} scatter diagram. Group B' oils show the expected result of an increasing Phytane/n-C_{18} ratio with decreasing Factor I content. However Group C oils which have the lowest Factor I content, and hence could have undergone the greatest extent of biodegradation, show decreasing Phytane/n-C_{18} ratios with decreasing Factor I values. This is contrary to the relationship expected from the biodegradation of these crude oils. Unfortunately, the Phytane/n-C_{18} ratio is sensitive to maturation, and the negative correlation of this ratio with Factor I values is also fully predictable from the thermal alteration of the crude oils. Until experimental data are compiled which characterize biodegradation and maturation processes using the slopes, intercepts and topologies of the Phytane/n-C_{18} scatter diagrams, such plots are only speculative and quite inconclusive.

There is other evidence which indicates that biodegradation is an unlikely process in the D-3 and Keg River reef system. In a paper by Winters and Williams (1969), the Bell Creek oil pool was stated to have been biodegraded principally by aerobes along the contact of the normal oil field brines with an influx of fresh oxygenated water. Such a hydrodynamic situation does not exist in the D-3 reservoir along either of the three reef trends sampled (Hitchon, 1969a and 1969b) or in the Keg River reefs at the Zama and Virgo fields. It is even more unlikely that the D-3 pools and Keg River pools can support a sulphate reducing bacteria population since these microbes require a tenuous symbiotic existance with aerobes, as the sulphate reducers cannot metabolize crude oil (Harwood, 1973 and Jobson, 1976). Furthermore, the sulphate reducing strains cultured from crude oils are dormant or killed at temperatures near 60°C. The lowest temperature pools studied, West Drumheller, Buffalo Lake and Big Lake have a present day reservoir temperature near this limit.

e) Oil Families

An oil family was defined by Marzec et al. (1971) as a group of crude oils which has undergone the same chemical metamorphism (maturation) and have been derived from the same source rocks. Although the preceding factor analysis did not adequately discriminate between Keg River and D-3 oils a substantial Factor III loading did separate three of the five Keg River oils from the majority of the D-3 oils. However, the identification of oils from different sources using this factor analysis was not satisfactory. Data reported by Deroo et al. (1977) indicate that the oils from the Homeglen-Rimbey-Redwater trend were derived from the surrounding Ireton and Duvernay shales. Since the Wimborne-Duhamel and Stettler-West Drumheller reefal pools have a similar geological setting, their oils were probably generated from these same source rocks. Furthermore, the D-3 reservoirs along these three reef trends have aquitards between them (Hitchon, 1969a and 1969b) and any significant secondary hydrocarbon migration between the trends would therefore be improbable. Consequently, the classification of the sulphur-poor oils from the Wimborne-Duhamel pools with the Homeglen-Rimbey-Redwater oils to form Group B' is evidence that these two reef trends contain oils which have been derived from the same source rocks. The continuum of Group B' and Group C oils along the Factor I - Factor II join (see Figure II - 3) is the result of the closure of the varimax factor loadings matrix, and the probable circumstance that these two oil groups are cogenetic but differ in composition due to varying extents of maturation and sulphurization. It is therefore likely that the D-3 oils from the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller reef trends form one oil family.

Section 2: Sulphur Isotopes of D-3 and Keg River Oils

The total sulphur content of the D-3 and Keg River oils was quantitatively extracted using the Parr Bomb procedure described in Part I, Chapter I of this thesis. The extracted sulphur was then converted to silver sulphide and oxidised to sulphur dioxide for sulphur isotope analysis (see Part I, Chapter I). The sulphur isotope data are reported in the δS^{34} notation and listed in Table II - XI. δS^{34} is defined as:

$$\delta S^{34} = \left(\frac{S^{34}/S^{32}\ \text{sample}}{S^{34}/S^{32}\ \text{standard}} - 1 \right) 1000$$

and has units of per mil (^{0}/oo). All sulphur isotope del values are quoted with respect to the meteorite standard Canyon Diablo troilite. A summary of sulphur isotope calibration and correction procedures and measurement reproducibility and accuracy is given in Part I, Chapters I and II of this thesis.

Figure II - 10 illustrates the sulphur isotope distribution for oil sulphur extracted from the Upper Devonian D-3 and Middle Devonian Keg River oils. Statistically speaking, the mean δS^{34} values of the sample oil populations taken from the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller D-3 pools are not significantly different. The mean sulphur isotope value and standard deviation

TABLE II - XI

Sulphur Isotope+ Values for Albertan Devonian Oils, Sour Non-Associated and Solution Gases, and Related Aqueous Sulphides and Brine Sulphates

Pool Name	Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Big Lake	D-3 13-25-53-26W4	+15.0	+14.4				
	9-26-53-26W4	+15.0	+13.6				
Acheson	D-3 4-10-52-26W4	+12.3					
Yekau Lake	D-3 8-4-52-26W4	+12.5					
Leduc Woodbend	D-3 13-3-50-26W4	+13.1					
	8-5-51-26W4	+13.2					
	8-9-50-26W4	+13.1					
Golden Spike	D-3 10-27-51-27W4	+15.2					
	12-26-51-27W4	+15.2					
Wizard Lake	D-3 1-21-48-27W4	+16.0					
Glen Park	D-3 4-2-49-27W4	+13.8					
	5-2-49-27W4	+13.1					

All δS^{34} values are given in reference to the Canyon Troilite Standard.

TABLE II - XI (Cont'd)

Pool Name	Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Bonnie Glen	D-3 14-6-47-27W4	+14.9					
Sylvan Lake	D-3 Separator Sample	+18.1	+17.5		+18.5	+18.3	+21.8
Westerose	D-3 Battery Sample	+15.0	+17.7 +17.7 +17.9				
West Drumheller	D-3 11-1-30-21W4	+5.5	+10.2				
	12-1-30-21W4	+5.6	+10.5				
New Norway	D-3 11-36-44-22W4	+10.2	+13.6				
Buffalo Lake	D-3 4-35-39-21W4	+17.2	+15.4	+14.7			
Bashaw	D-3 10-6-42-22W4	+14.5	+15.8	+14.7			
Erskine	D-3 2-7-39-20W4	+17.4	+15.4				
	6-19-39-20W4	+17.0	+15.2				
	8-13-39-21W4	+17.1					+21.0
	8-26-39-21W4	+16.5	+15.2	+15.1			
Stettler	D-3 12-3-38-20W4	11.9	14.5				
	16-9-38-20W4	11.9	14.4				
	16-16-38-20W4	12.6	14.4				

TABLE II - XI (Cont'd)

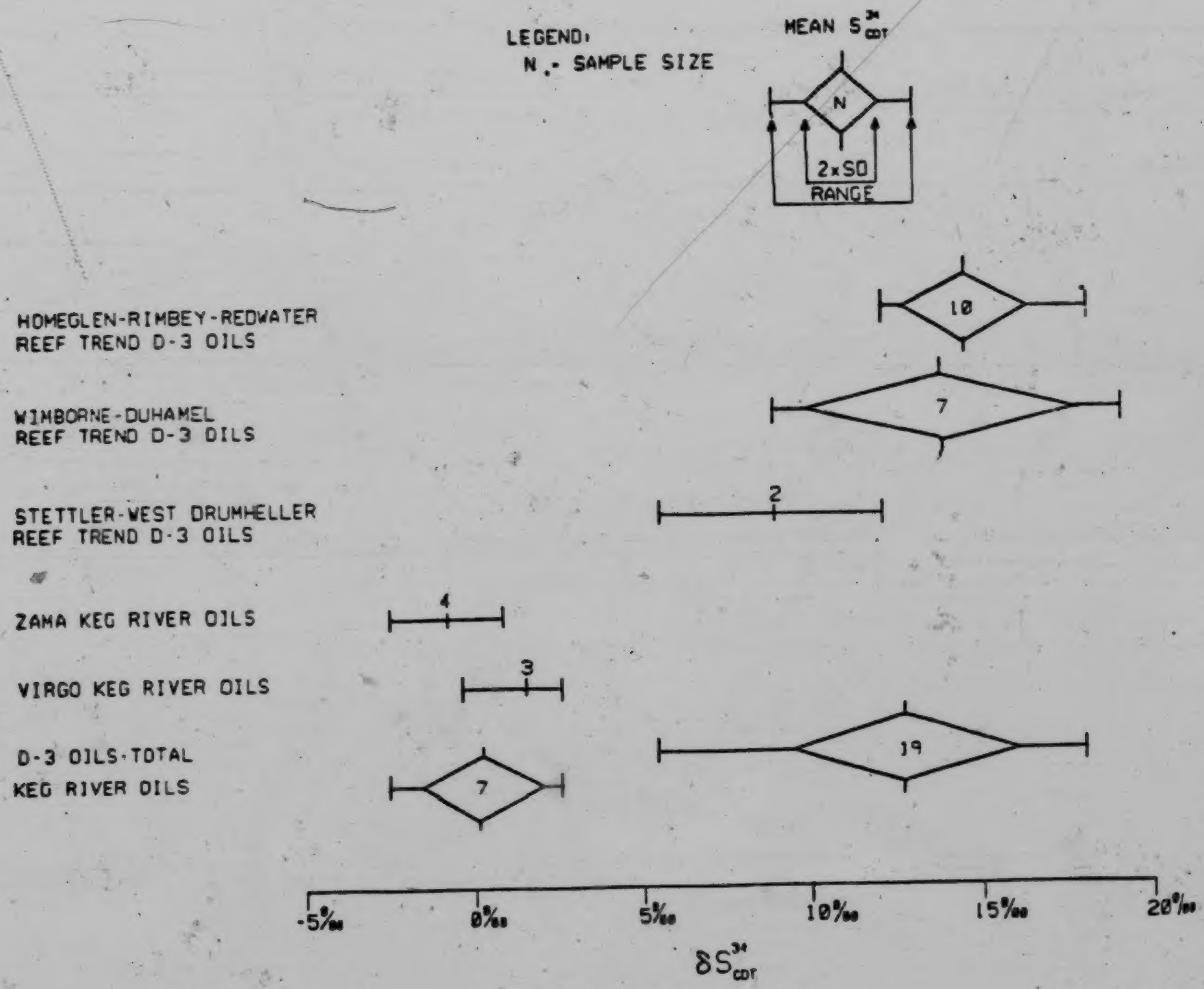
Pool Name	Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Malmo	D-3 5-14-44-22W4	+8.9	+16.0				
	2-23-44-22W4	+8.7	+15.7				
Clive	D-3A 16-29-40-24W4	+9.9	+15.8				
	12-33-40-24W4	+10.1	+15.5	+15.5			
Wimborne	D-3 4-1-33-26W4		+16.3				
	6-11-33-26W4	+18.9					
	7-26-33-26W4		+16.4	+16.3			
Zama Keg River	6-23-116-4W6	+0.9					
	7-7-116-5W6	+0.2	+5.5				
	4-36-116-6W6	-2.5	+10.4				
	12-21-117-4W6	-1.3	+5.1				
	2-25-117-5W6	+0.2	-0.5				
Virgo Keg River	4-6-115-5W6	-0.3	+5.5				
	5-11-115-5W6	+2.3					
	5-27-115-5W6	+2.5	+14.6				
Rainbow Keg River	8-32-111-7W6	+6.8					
Non-Associated Gases							
Ricinus	D-3 7-13-36-10W5		+20.4	+20.4			
	10-33-36-10W5		+20.5				

TABLE II - XI (Cont'd)

Pool Name	Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Non Associated Gases - Cont'd							
Strachan	D-3 10-31		+20.6				
	7-32		+20.7				
Harmatten E.	D-3 #1		+23.0				
	#2		+22.6	+22.4			
Pine Creek	D-3 10-16		+22.2			+25.0	
	10-23		+22.7	+22.0			
Pine N. W.			+23.0				

FIGURE II-10

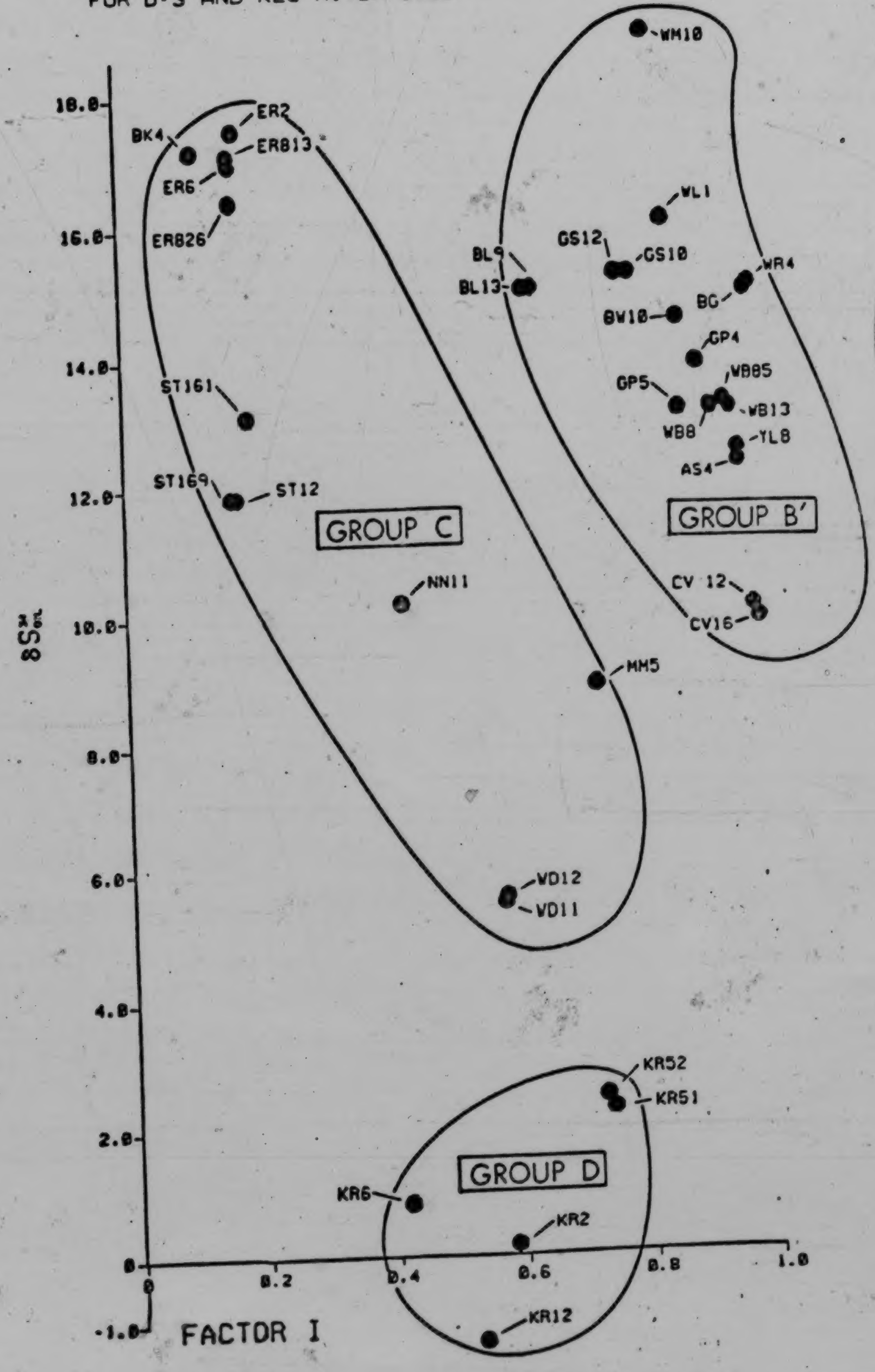
SULPHUR ISOTOPE VALUES FOR DEVONIAN OILS
IN ALBERTA



determined from 19 D-3 oils in this study is + 13.7, ± 3.4°/oo. This mean value is comparable to the sulphur isotope composition for 10 Leduc reef oils, from the same oil population, determined by Thode _et al_. (1958) to be + 12, ± 1.8°/oo. The mean and standard deviation for the Middle Devonian Keg River oils sampled at the Zama-Virgo field is + 0.3, ± 1.8°/oo. Statistically speaking, the sulphur isotope composition of the Keg River and D-3 oils is different. In Figure II - 11 the sulphur isotope composition of the oils has been plotted against the Factor I component. Group C and Group B' oils are defined as before (see Figure II - 6) with the exception that the Malmo oil is included with Group C. A fourth group of oils, D, from the Middle Devonian Keg River formation, is also defined. The statistically significant negative linear correlations between δS^{34} and Factor I for Group B' and Group C oils can be interpreted to indicate that the variation in the sulphur isotopic content of oil sulphur is controlled by maturation and sulphurization.

Since the D-3 oil sample population was chosen to include extreme stages of maturation and sulphurization, the fact that the D-3 sulphur isotope population is statistically different from the Keg River δS^{34} population is a good indication that the sulphur source for the Keg River and D-3 oils is different. Furthermore, the similarity in the sulphur isotope composition between the Group C oils and Group B' oils indicates that the oils from the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller reef trends have the same general

FIGURE II-11
PLOT OF δS^{34} vs FACTOR I CONTENT FOR D-3 AND KEG RIVER OILS



sulphur source.

According to Thode _et al_. (1958) and Thode and Monster (1965) the sulphur source for crude oil is ocean sulphate. Through the process of bacterial sulphate reduction, contemporaneous ocean sulphate is reduced to hydrogen sulphide which can then interact with organic matter in the source sediments during very early diagenesis, producing immature organosulphur compounds. The definition of an absorbed hydrogen sulphide phase in source rocks by Le Tran (1971) and Le Tran _et al_. (1973) suggests that the sulphurization of oils could occur during their genesis over a more favorable temperature range (80 - 175°C). Possible sources of the absorbed hydrogen sulphide are: early bacterial sulphate reduction (Thode _et al_. 1958; Thode and Monster, 1965); thermal decomposition of originally sulphur-rich plant material (Le Tran, 1971); and abiogenic chemical reactions between hydrogen sulphide, hydrocarbons and pore-water sulphate during petroleum genesis. However, as noted by Bestougeff and Combaz (1973) the sulphurization of petroleum is chemically possible at all stages of its formation and entrapment. The ability of hydrocarbons, aqueous sulphate and hydrogen sulphide to participate in a Toland type chemical reaction (Toland, 1960; see also Part II, Chapter I and Part II, Chapter III) and generate an abundance of reactive reduced valence state sulphur compounds gives the oil sulphurization process an equal probability of occurring in either the source rocks or in the reservoir. Furthermore, oils from the same family (see Part II, Chapter II, Section 1d) can have a wide range (14^{o}/oo) in sulphur isotope composition (see Figure II - 10) due to maturation and sulphurization reactions. Consequently, using the δS^{34} value of crude oils to define a petroleum source or to relate crude oils from the same source could be misleading. For example, there is little difference, on a statistical basis, between the sulphur isotope frequency distributions for the Middle Devonian Keg River oils from the Zama-Virgo field (mean = 0.3^{o}/oo, SD = 1.8) and for the Upper Cretaceous oils (mean = 2.9^{o}/oo, SD = 1.9) analysed by Thode _et_ _al_. (1958). However, the conclusion, based on sulphur isotope similarity, that the Upper Cretaceous and Middle Devonian oils have the same source rocks would be premature due to the fact that the two oils are separated geographically by some 500 miles and separated stratigraphically by two major aquitards, the Beaverhill Lake - Ireton shales and Muskeg evaporites. The sulphur isotope composition of a statistically meaningful sample population of crude oils is best used in conjunction with other parameters (see Erdman and Morris, 1974) for the correlation of crude oils.

The relationship defined in Figure II - 11 is a decreasing δS^{34} value with increasing Factor I content for Group B' and Group C oils. Using the correlation equations calculated for the plot of Factor I against present day reservoir temperature (see Figure II - 4) the sulphur isotope values of the Group B' and Group C oils can be related to an average temperature+ which is solely a maturation parameter. The correlation coefficient (r) for the linear correlation of $_{\delta}S^{34}$ against the average maturation temperature (AMT) is -0.25 for the Group B' oils and +0.89 for the Group C oils (see Figure II - 12). Only the correlation for the Group C oils is statistically significant at the 5% level of confidence. The positive correlation between $_{\delta}S^{34}$ and the maturation parameter (AMT) for the Group C oils agrees with the trend observed by Orr (1974) who noted an increase in mean $_{\delta}S^{34}$ value as oil group maturity increased. The Group C oils and the Paleozoic Big Horn Basin oils, analysed by Orr (1974), are high sulphur varieties with sulphur in excess of 0.9%. With the exception of the Wimborne pool, Group B' oils have sulphur contents less than 0.9% and generally less than 0.5%. Therefore the different correlations between $_{\delta}S^{34}$ and average maturation temperature, observed for the low sulphur Group B' and high sulphur Group C oils, suggests that these two groups have undergone different sulphurization-desulphurization reactions and/or experienced different sulphurization - desulphurization histories.

+The equations used to calculate the average maturation temperature (AMT) are:

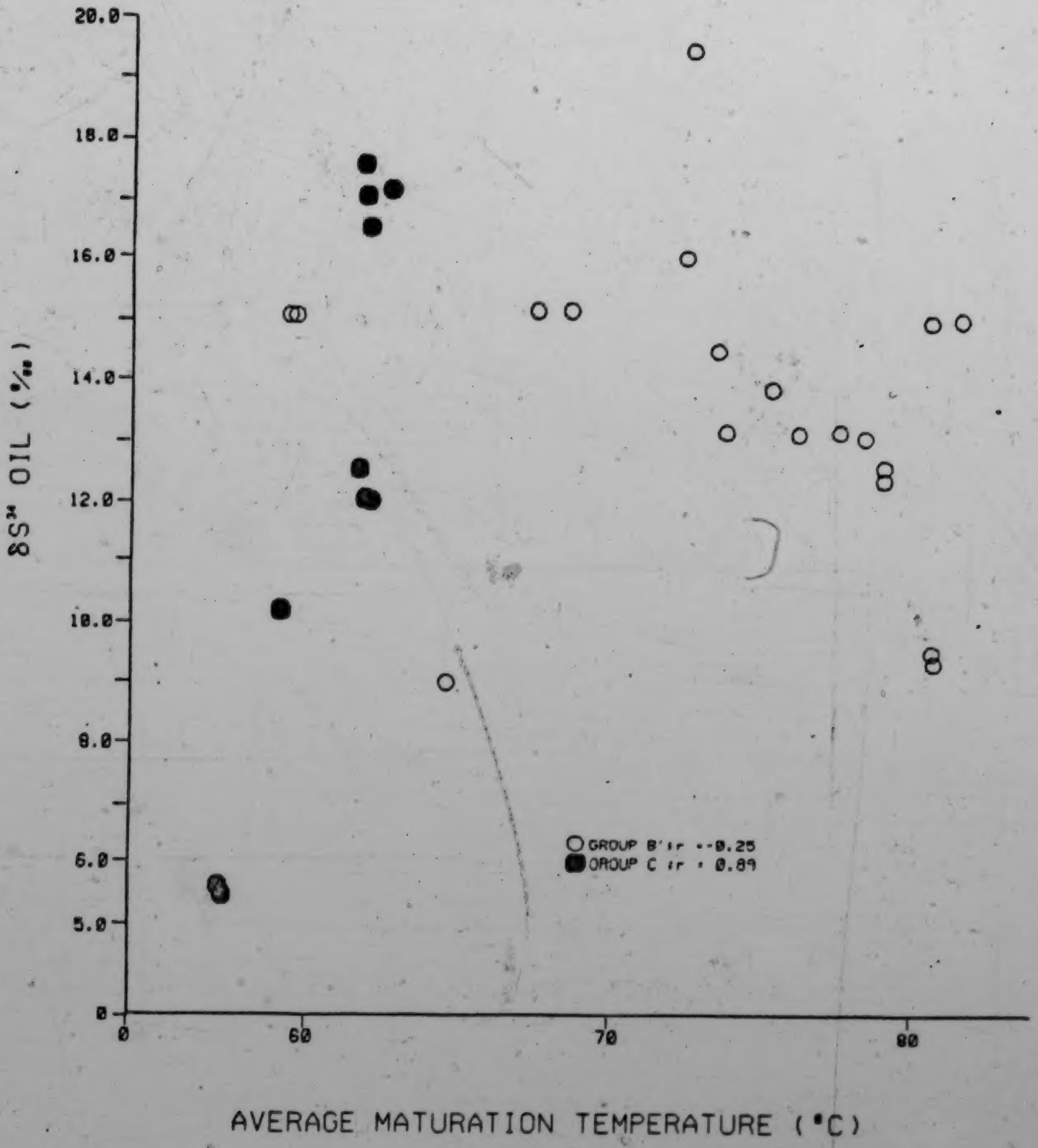
1) AMT = 62.04 Factor I + 19.38 Group B'

2) AMT = 11.66 Factor I + 63.93 Group C

(see Figure II-4)

FIGURE II - 12

PLOT OF δS^{34} vs AVERAGE MATURATION TEMPERATURE FOR D-3 OILS. R IS THE LINEAR CORRELATION COEFFICIENT

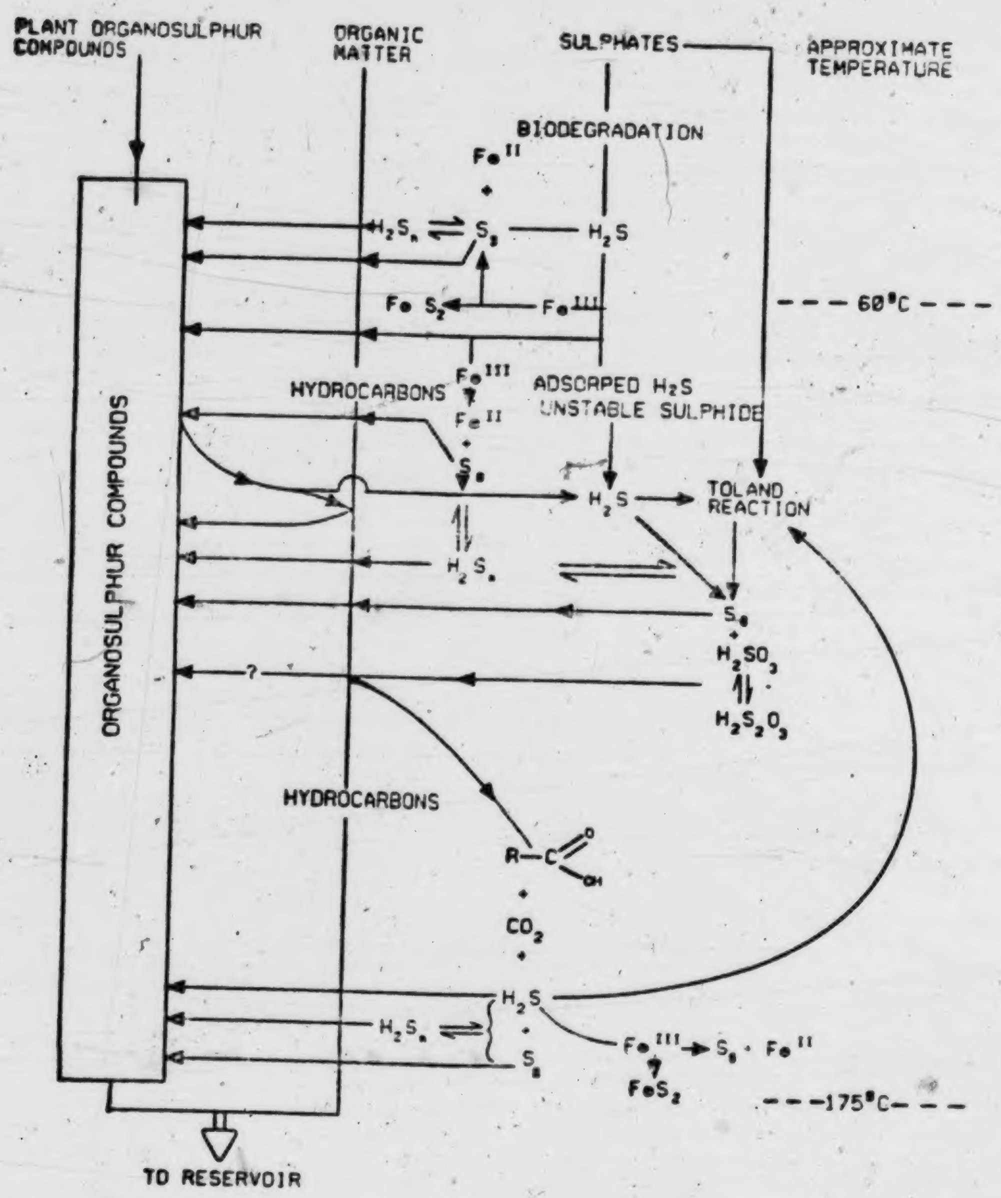


The sulphurization and desulphurization reactions and concomitant sulphur isotope fractionations for a crude oil are of unknown complexity. The reaction rates, reacting species and products, reaction mechanism and isotope fractionation factors involved, are only known in general. In Figure II - 13 and Figure II - 14 general reaction paths are outlined for the oil sulphur system.

In the source rocks a variety of inorganic sulphur compounds (sulphurizing reagents) can be produced by two main classes of reactions, biodegradation and maturation (refer to Figure II - 13). During the early stages of source rock diagenesis, at temperatures less than 60°C, the bacterial reduction of pore water sulphate (refer to Oppenheimer and Broneer, 1963) would generate primarily hydrogen sulphide which through a series of secondary reactions could produce reduced transition metal cations, bisulphide, native sulphur and polysulphides (Berner, 1963). These sulphur compounds can then react with organic matter to produce a variety of immature sulphur species characterized by nonthiophenic sulphur compounds and benzothiophenes (Ho et al. 1974). The sulphur isotope composition of the immature organosulphur compounds would be a function of the δS^{34} value of the source sulphate, the kinetic isotope fractionation factor established during the biological reduction of sulphate (Harrison and Thode, 1957; Kemp and Thode, 1968), the equilibrium fractionation factor established between the H_2S, HS^-, H_2S_n, S_8 species at reservoir temperature (Berner, 1963; Sakai, 1968), the mole fraction of the various

FIGURE II - 13

GENERALIZED SOURCE ROCK SULPHUR SYSTEM


PLANT ORGANOSULPHUR COMPOUNDS
ORGANIC MATTER
SULPHATES
APPROXIMATE TEMPERATURE
BIODEGRADATION
Fe II
H2Sn
S8
H2S
Fe S2
Fe III
60°C
Fe III
Fe II
HYDROCARBONS
ADSORPED H2S
UNSTABLE SULPHIDE
S8
H2S
TOLAND REACTION
ORGANOSULPHUR COMPOUNDS
H2Sn
S8
H2SO3
H2S2O3
?
HYDROCARBONS
R-C O OH
CO2
H2S
H2Sn
S8
Fe III
S8 · Fe II
FeS2
175°C
TO RESERVOIR

sulphurizing reagents (Ohmoto, 1972) the sulphur isotope fractionation factor(s) (at reservoir temperature) for the kinetic or equilibrium reaction(s) which produced the organic sulphur compounds and the extent of depletion of the source sulphur (sulphate) supply. A portion of the biogenically derived sulphurizing agents could be retained as an absorbed phase (Le Tran, 1971; Le Tran et al. 1973) or as an unstable transition metal sulphide (Berner, 1962, 1964, 1967, 1969, 1970) which could serve as a potential sulphur source for later (higher temperature) reactions. At higher source temperatures (greater than 60°C) a Toland type reaction between sulphate and hydrogen sulphide (Toland, 1960) would produce an abundance of sulphurizing reagents (H_2S, $H_2S_2O_3$, H_2SO_3, S_8, H_2S_n) which are capable of reacting with organic matter and newly formed hydrocarbons to produce immature or mature (depending on source temperature) sulphur compounds (refer to Ho et al, 1974). The controls on the sulphur isotope composition of the organosulphur compounds are essentially the same as those for the biogenetically related organosulphur species except that the fractionation factor for the initial reduction of sulphate is not established through biochemical reaction mechanisms. The magnitude of the fractionation factor may be essentially the same since both involve kinetic reduction mechanisms with probably similar rate controlling steps (Harrison and Thode, 1957). Since the reaction rates for the generation of the sulphurizing reagents and organosulphur compounds are temperature dependent (doubling or tripling for about every 10°C increase in temperature) the mole fraction of sulphur species produced and its sulphur isotope composition would be temperature dependent. Some of the organosulphur compounds in the source have been inherited from the original organic matter. Their sulphur isotope composition would be close to the contemporaneous sea water sulphate value (Kaplan et al. 1963; Midge, 1953). As a result, the sulphur isotope composition of the petroleum phase collecting in the reservoir, just after primary migration, would be an average value determined by the δS^{34} value of each organosulphur species present weighted by its mole fraction. Since the organosulphur species, its mole fraction and its sulphur isotope composition vary with source temperature, the overall sulphur isotope composition of this oil phase would vary as the source temperature changed with increasing overburden thickness and increasingly heat flux related to geosynclinal - subduction zone activity.

Once in the reservoir system the crude oil phase is free to migrate and collect in a suitable trap to form an oil pool. If the oil phase forms a "slug" (refer to Levorsen, 1967) its sulphur isotope composition defined in the source should be retained throughout the secondary migration stage. However if the organosulphur compounds migrate as micells or in some solubilized molecular form (refer to Baker, 1967; and Price, 1976) further sulphur isotope fractionation could result from diffusion.+ The concept of an initial sulphur isotope composition for an oil pool is useful but illusory since oil accumulation in a trap can be a continuing process correlative with the period of time

---

+ According to H. R. Krouse (personal communication), any oil sulphur isotope fractionation which results from micellar diffusion should be minimal.

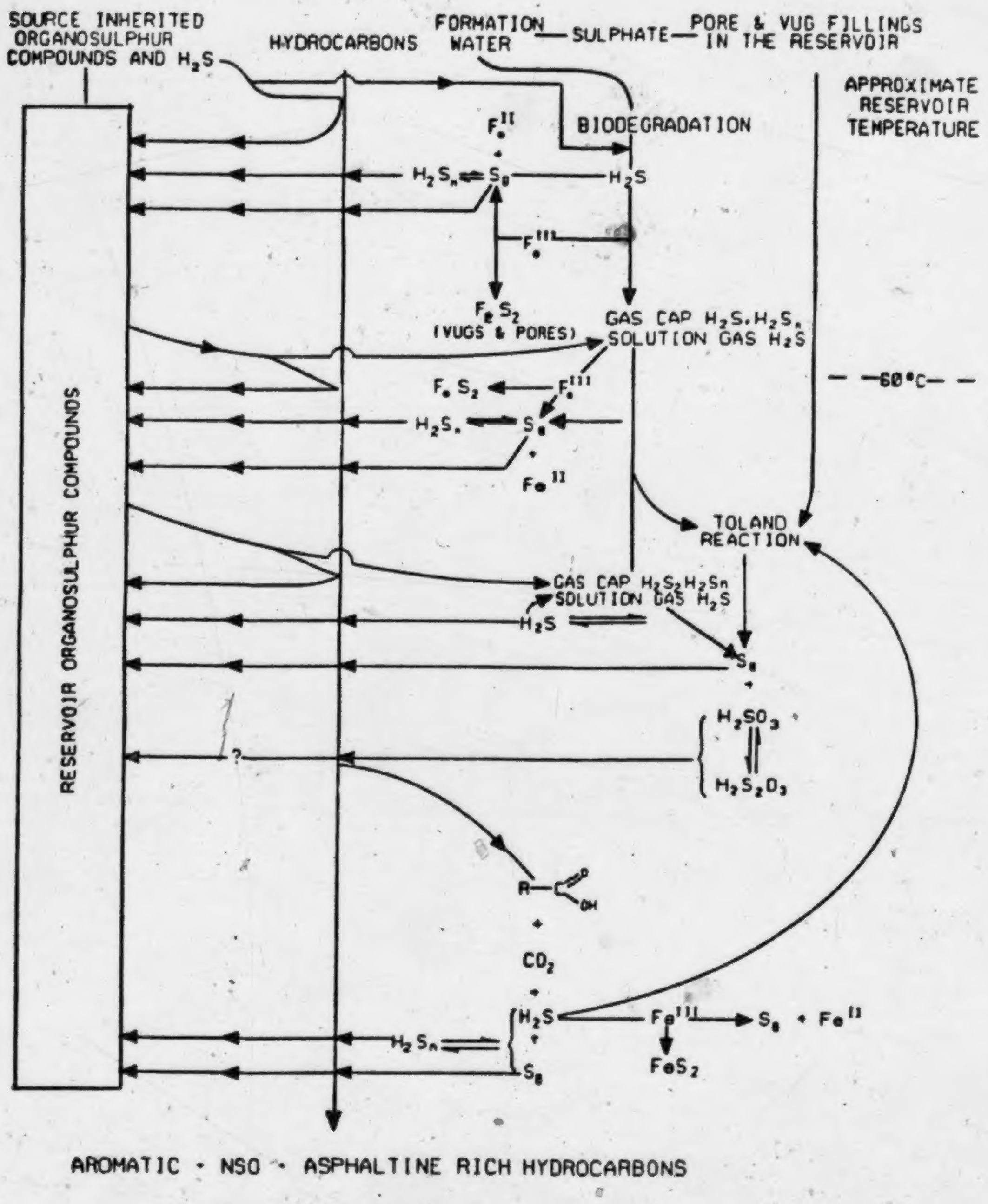
required to pass the source rocks through the oil generation window (refer to Biederman, 1975). Also, after the source has passed its oil generation capacity, oil can be redistributed within the reservoir through displacement by gas migrating up dip from the metamorphosed source rocks (refer to Gussow, 1954). The oil pools that are affected by gas displacement probably form a minority; for example, of the 18 D-3 oil pools sampled in this study, only 5 show evidence of gas displacement. Then, in a general sense, the initial δS^{34} value of an oil pool is achieved during the period of the most significant accumulation of organosulphur compounds. This probably coincides with the maximum phase of oil generation - migration in the source. The concept of an initial sulphur isotope composition is made even more nebulous by an in situ reaction, accompanied by sulphur isotope fractionation effects, between hydrocarbons and source-derived sulphanes during or before the arrival of the organosulphur compounds from the source.

Once the oil pool has achieved its initial sulphur isotope composition, this can be modified within the reservoir - trap by three main types of reactions (refer to Figure II - 14). These are:

1) biogenic sulphurization reactions
2) abiogenic sulphurization reactions
3) desulphurization (thermal decomposition) reactions

FIGURE II - 14

GENERALIZED RESERVOIR SULPHUR SYSTEM


SOURCE INHERITED ORGANOSULPHUR COMPOUNDS AND H_2S
HYDROCARBONS
FORMATION WATER
SULPHATE
PORE & VUG FILLINGS IN THE RESERVOIR
APPROXIMATE RESERVOIR TEMPERATURE
BIODEGRADATION
Fe^{II}
H_2S_n
S_8
H_2S
Fe^{III}
FeS_2 (VUGS & PORES)
GAS CAP $H_2S.H_2S_n$ SOLUTION GAS H_2S
— 60°C —
FeS_2
Fe^{III}
H_2S_n
S_8
Fe^{II}
RESERVOIR ORGANOSULPHUR COMPOUNDS
TOLAND REACTION
GAS CAP $H_2S_2H_2S_n$ SOLUTION GAS H_2S
H_2S
S_8
?
H_2SO_3
$H_2S_2O_3$
R—C(=O)OH
CO_2
H_2S
H_2S_n
S_8
Fe^{III}
S_8 + Fe^{II}
FeS_2
AROMATIC - NSO - ASPHALTINE RICH HYDROCARBONS

If reservoir temperatures were low (less than 60°C) and the hydrodynamics of the reservoir system suitable (refer to Winters and Williams, 1969) bacterial hydrogen sulphide and related elemental sulphur and sulphanes could be produced. The resultant reactions between these sulphurizing agents and petroleum would produce a variety of organosulphur compounds characteristic of the altered oil group defined by Ho et al. (1974). The δS^{34} value of the bacterial hydrogen sulphide would, on the average, be some 40‰ lighter (more S^{32} enriched) than the parent sulphate (H. R. Krouse, personal communication). Equilibrium reactions between H_2S, HS^-, S_8 and polysulphide (Berner, 1963) could produce a further 12‰ S^{32} enrichment (Sakai, 1968; Tudge and Thode, 1950). Therefore, on the average, sulphurizing reagents some 52‰ lighter than the parent sulphate would be expected from the bacterial sulphur system.+ Further sulphur isotope fractionation is quite probable during the oil sulphurization reactions by biogenic sulphur, but the magnitude of these fractionation factors is not known. At reservoir temperatures over a range from approximately 60 to 175°C, a reaction between sulphate and hydrogen sulphide (Toland, 1960) is capable of producing a variety of sulphurizing reagents ($H_2S_2O_3$, H_2SO_3, S_8, H_2S, H_2S_n). The reaction between these and petroleum would produce an oil enriched in aromatics, total sulphur and asphaltenes (Pryor, 1962; Gousseva and Fainguerch, 1973). Rates of a chemical reaction are related exponentially to temperature through the relationship between the rate constant and temperature defined in the Arrhenius equation (refer to Barrow, 1966). Therefore,

---

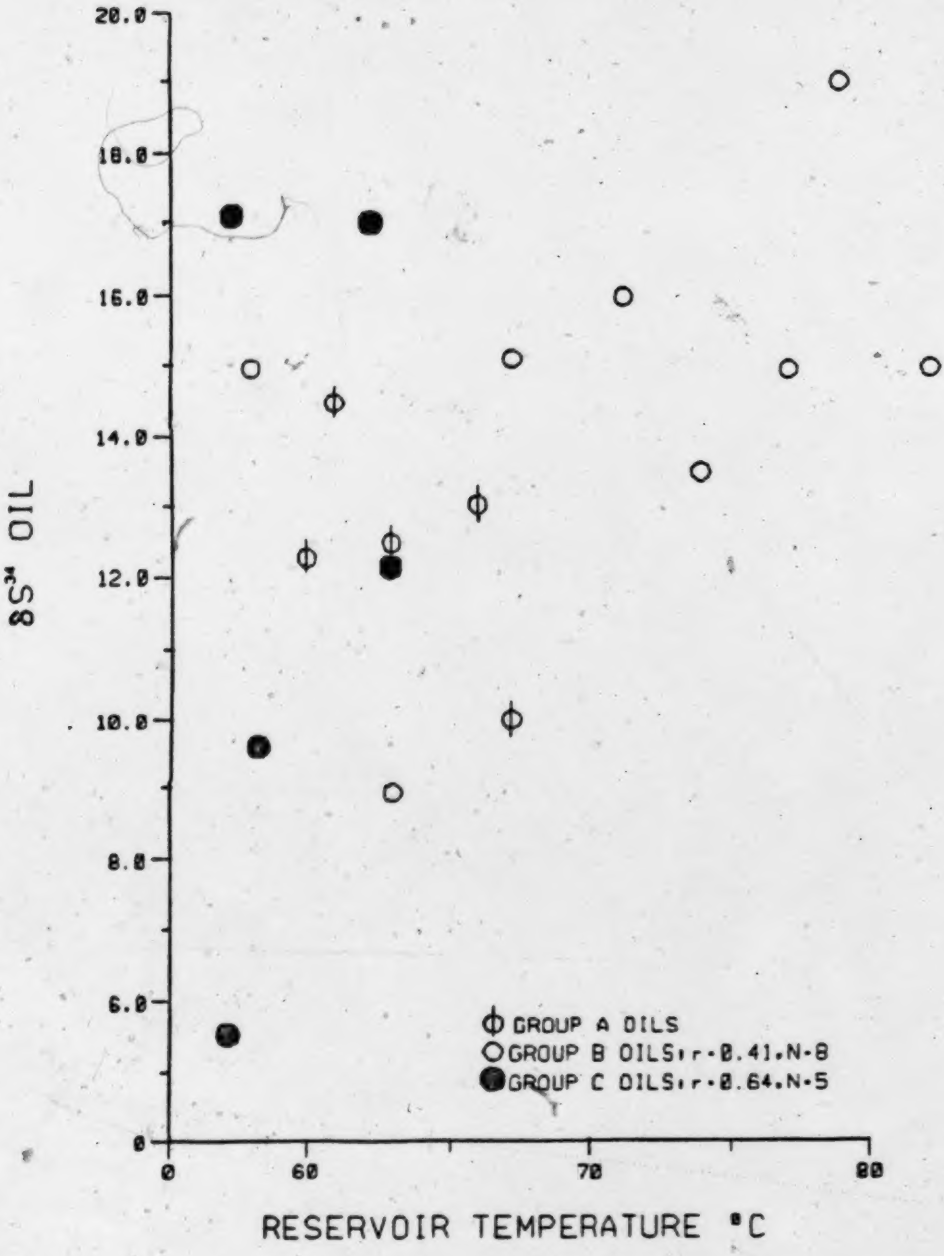
+ Bacterial sulphide also exhibits a large range in δS^{34} values.

for a reaction between petroleum and a sulphurizing reagent, the types, mole fractions and sulphur isotope compositions of the organosulphur compounds produced would depend significantly on reservoir temperature. The sulphur isotope composition of the total oil sulphur would depend on the mole fraction and sulphur isotope composition of the source-inherited and newly produced organosulphur compounds. However, the prolific nature of the Toland reaction (Toland, 1960) would eventually result in the δS^{34} value of the total oil sulphur being controlled, through dilution, by the sulphur isotope composition of the organosulphur compounds produced by the reservoir sulphurization reactions. In the case where no sulphate occurs in the reservoir, any sulphurization of the oil phase would result from a reaction with the H_2S - H_2S_n - S_8 group of reagents which have migrated from the source. However, the very reactive nature of these compounds together with an abundance of reactive sites (transition metal cations, clay mineral surfaces, unsaturated organic compounds) within the source rocks could result in the retention of most of the source-generated sulphurizing reagents. Therefore, the sulphur system history of oils which are precluded from participating in a "Toland type" reaction is probably dominated by the thermal decomposition of source-inherited organosulphur compounds and the transformation of these into more stable sulphur compounds suited to higher temperatures. The types of organosulphur compounds which characterize crude oils undergoing desulphurization reactions are probably typical of the mature and mercaptan rich oil groups discussed by Ho et al. (1974). The sulphur isotope composition of oils undergoing desulphurization would depend on the δS^{34} value of the source inherited organosulphur compounds, the mole fraction of the oil sulphur compounds present, the sulphur isotope fractionation factors for the various desulphurization reactions and the fraction of sulphur lost, as insoluble NSO compounds and gaseous sulphides, from the oil.

In the preceding discussion of the oil sulphur system, the point was made that the isotope composition of oil sulphur should be a function of reservoir temperature due to the control that temperature has on the reaction rates and isotope fractionation factors of the sulphurization and desulphurization reactions. Consequently, for the Group C oils (West Drumheller, New Norway, Stettler, Buffalo Lake and Erskine) the excellent positive linear correlations between δS^{34} and AMT (see Figure II - 12) and δS^{34} and Factor I (see Figure II - 11) together with the low content of Factor I for these oils supports the concept of an oil composition controlled by sulphurization reactions. The inability of the plot of δS^{34} vs present day reservoir temperature to define oil groups A, B or C (see Figure II - 15) and, for the Group B' oils, the independent relationship between δS^{34} and AMT (see Figure II - 12) is not consistent with a straightforward relationship between the sulphurization process and reservoir temperature. A final synthesis of the oil sulphur system will be presented following the discussion of the sulphur isotopes of the natural gases in the next chapter.

FIGURE II - 15

PLOT OF POOL AV. δS^{34} VALUE vs PRESENT DAY RESERVOIR TEMPERATURE



Section 3: Carbon Isotopes of D-3 and Keg River Oils

Oil samples and their saturate and aromatic fractions were converted to carbon dioxide, for carbon isotope analysis, using the wet oxidation and Carius tube methods described in Part I, Chapter I. Carbon isotope ratios are given as δC^{13} values referenced to the Chicago standard Belemnitella americana from the Upper Cretaceous Pee Dee Formation. δC^{13} is defined as:

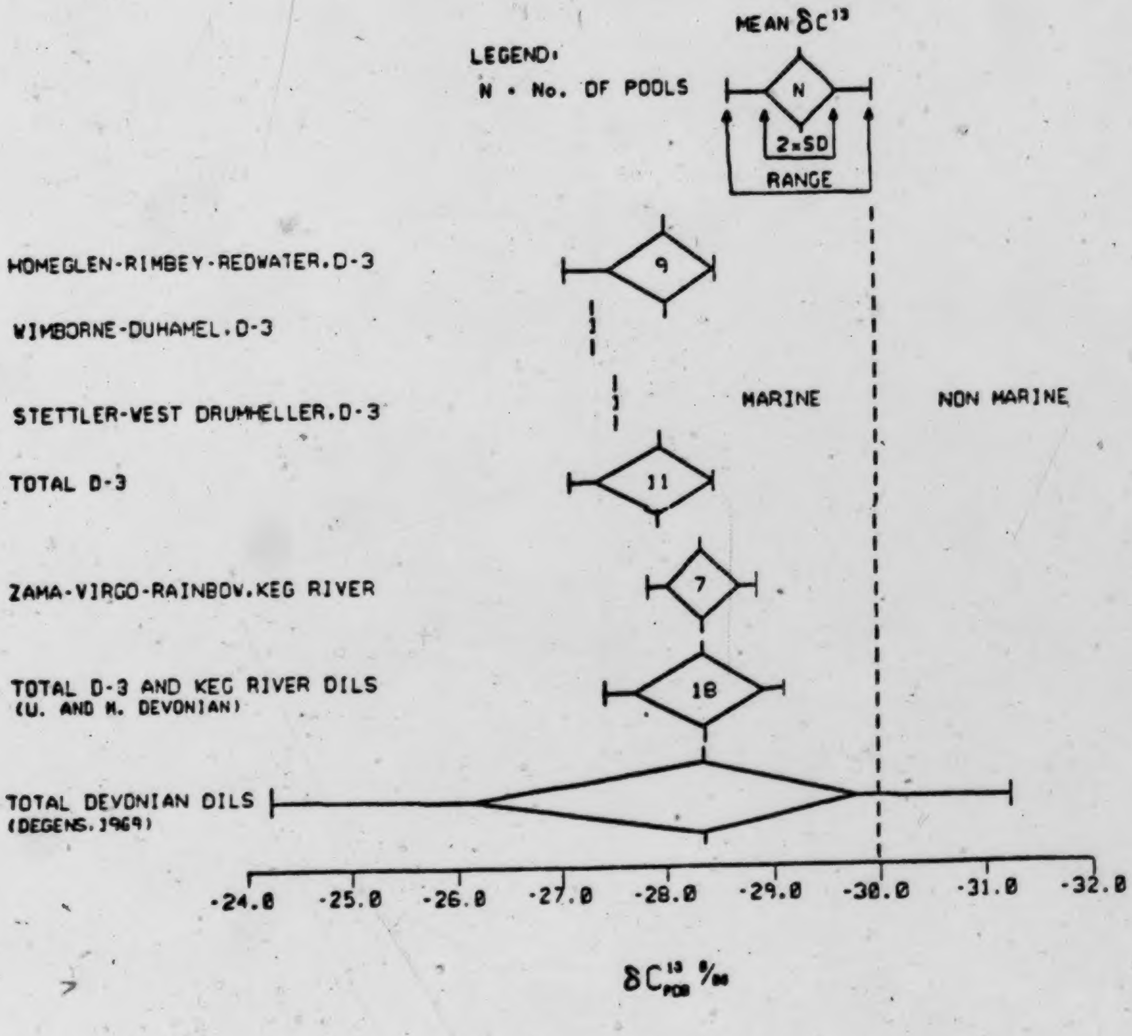
$$\delta C^{13} = \left(\frac{C^{13}/C^{12} \text{ sample}}{C^{13}/C^{12} \text{ standard}} - 1 \right) 1000 \text{ and has units of}$$

per mil ($^{o}/oo$). A summary of the δC^{13} values for the D-3 and Keg River oils is given in Appendix II - II. Carbon isotope calibration and correction procedures, and measurement reproducibility and accuracy are discussed in Part I, Chapters I and II of this thesis. Since the carbon isotope determination for whole oils was finished prior to the completion of the sample programme, only a portion of the wells have whole oil δC^{13} values.

The mean and range of carbon isotope analyses ($-28^{o}/oo$ and $-27.2^{o}/oo$ to $-28.7^{o}/oo$) for oils from the Upper Devonian D-3 and Middle Devonian Keg River formations (refer to Figure II - 16) indicate that these oils have been generated from marine source rocks (Silverman, 1964; Silverman, 1967) of Devonian age (Degens, 1969). This conclusion is in

FIGURE II·16

CARBON ISOTOPE VALUES FOR D-3 AND KEG RIVER OILS IN ALBERTA



agreement with a source rock study reported by Deroo et al. (1977). Without exception, the saturate fraction of the D-3 and Keg River oils analysed was more enriched in C^{12}, by an average value of 1.8 ± 0.59^{o}/oo, than the aromatic fraction, in general agreement with data published by Galimov et al. (1970) and Burns et al. (1975). This prevalent C^{12} enrichment must reflect a fundamental, though probably quite complex, chemical relationship between the saturate and aromatic oil fractions. The C^{12} enrichment could have been inherited from the parent (pre oil genesis) organic compounds in the source and then modified during oil generation, migration and maturation, or established by these latter three processes.

Speaking strictly in terms of maturation, a possible rationale for the carbon isotope difference between the aromatic and saturate fractions is provided by a general maturation equation defined by Reznikov (1967) as:

$$\text{Napthenes} \longrightarrow \text{Paraffins} + \text{Aromatics}$$

A synthesis of this equation using first order kinetic reactions has successfully determined the chemical age of a crude oil (Reznikov, 1967; Young et al. 1977). In view of this maturation equation, a more meaningful carbon isotope relationship between the oil fractions could be defined by considering the napthenes and paraffins separately rather than as their grouped fraction, the saturates. Analysis of the saturate fraction results in the combination of a reactant (napthene), whose original δC^{13} value was probably close to the whole oil value, with a C^{12} - enriched product (paraffin). The resulting carbon isotope value is therefore only an average reflecting both reactants and products. However, this value is still sensitive to the factors which affect the fractionation of carbon isotopes during maturation. Due to time restrictions and analytical problems, the saturate fraction was not split into its napthene and paraffin portions.

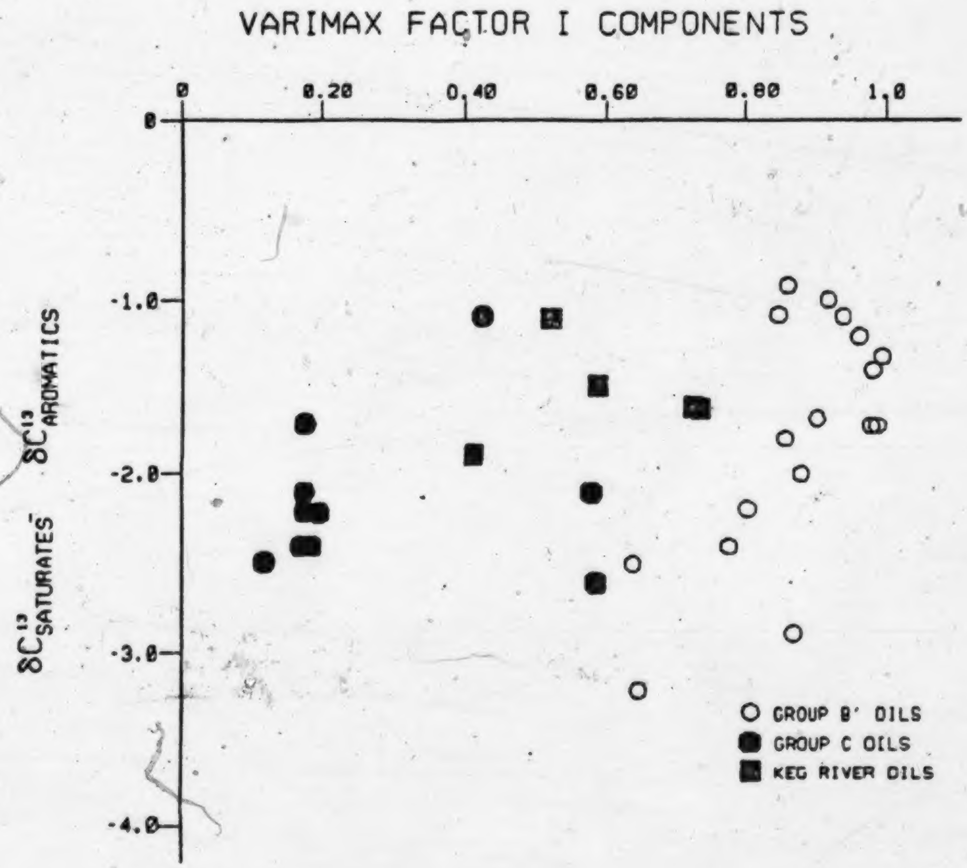
In Figure II - 17 the plot of the difference in δC^{13} values between the saturate and aromatic oil fractions against Factor I oil contents shows the variation of a carbon isotope quasi-enrichment factor with degree of maturation. The enrichment factor (Δ) is defined as:

$$\Delta_{A-B} = \delta_A - \delta_B \;/\; 1 + \frac{\delta_B}{1000} \quad \text{(Bottinga, 1968)}$$

The approximation $\Delta_{A-B} = \delta_A - \delta_B$ can be used without incurring significant error. Since the δC^{13} value of the saturate fraction and not the paraffin or napthene group was used, $\Delta_{SAT-ARM}$ is sensitive to mole fractions of napthenes and paraffins and as a result cannot be directly related to the isotope fractionation factor . Therefore this carbon isotope enrichment factor represents only indirectly an average of several kinetic and/or equilibrium fractionation factors defined by the chemical reactions implied in the general oil maturation equation defined by Reznikov (1967). The carbon isotope enrichment factor (Δ)

FIGURE II - 17

PLOT OF δC^{13} (SATURATES) - δC^{13} (AROMATICS) vs VARIMAX FACTOR I COMPONENTS FOR D-3 AND KEG RIVER OILS



is related to the isotope fractionation factor (α) through the following equation:

$$\Delta = 1000\ (\alpha - 1)$$

According to the thermodynamic principles discussed by Urey (1947), Tudge and Thode (1950), Harrison and Thode (1957) and Sakai (1968) the magnitude of the isotope fractionation factor diminishes with increasing reaction temperature in both equilibrium and kinetic systems. In Figure II - 17 the carbon isotope enrichment factor between the saturate and aromatic oil fractions has been plotted against the varimax Factor I content of the Devonian oils studied. The resulting significant positive linear correlation ($r = 0.44$, $N = 34$) indicates that the chemical reactions that produced the C^{12} enrichment in the saturate fraction probably conform to thermodynamic principles, in agreement with Reznikov (1967). However, the scatter of data in Figure II - 17 is so great that the carbon isotope values from the entire Devonian oil population are of little value for the identification of possible chemical reaction paths that could have caused the observed isotope fractionation between the saturate and aromatic oil fractions. If the data from Group B' oils are treated separately (see Figure II - 17) the scatter of the plotted values is narrow enough to give tolerable standard errors for the estimated Factor I contents ($\pm$ 0.0766) and carbon isotope enrichment factors ($\pm$ 0.49^{o}/oo). The correlation between the carbon isotope enrichment factors (Y) and varimax Factor I contents (x), ($x = 0.112Y + 1.071$ and

$Y = 4.387x - 5.588$) is satisfactory enough for the Group B' oils ($r = 0.70$, $N = 18$) to try and determine the isotope fractionation effects involved in maturation process from a theoretical and experimental approach using a simplified model such as the one defined by Reznikov (1967).

In Figures II - 18, II - 19 and II - 20 the δC^{13} values of the saturate and aromatic oil fractions and δC^{13} value of the whole oil have been plotted against Factor I. Both oil fractions and the whole oil, particularly for the Group B' crudes, show a significant enrichment in C^{12} with increasing extents of maturation (content of Factor I). Using a semi-theoretical argument Silverman (1964, 1967) concluded that cracking of source organic matter should produce C^{12} - enriched hydrocarbons (especially methane) and a heavy (C^{13} - enriched) condensed residue. Due to a closed system effect (refer to Broecker and Oversby, 1971 and Kemp and Thode, 1968) progressive maturation of the source would produce hydrocarbons that were successively more C^{13} enriched compared to earlier produced varieties (Silverman, 1967). Furthermore, data from experiments by Sackett (1968), Sackett _et_ _al_. (1968), Frank and Sackett (1969) and Frank _et_ _al_. (1974) in which crude oils were cracked to methane gas, indicate that the carbon isotope fractionation factor for a temperature range of 100° to 200°C is approximately 1.062, methane gas being enriched in C^{12}. Carbon isotope analyses on progressively more mature sulphur rich oils from the Big Horn Basin, reported by Orr (1974), indicate a C^{13} enrichment of the whole oil with

FIGURE II - 18

PLOT OF δC^{13} (SATURATE FRACTION) vs THE VARIMAX FACTOR I COMPONENT FOR KEG RIVER AND D-3 OILS

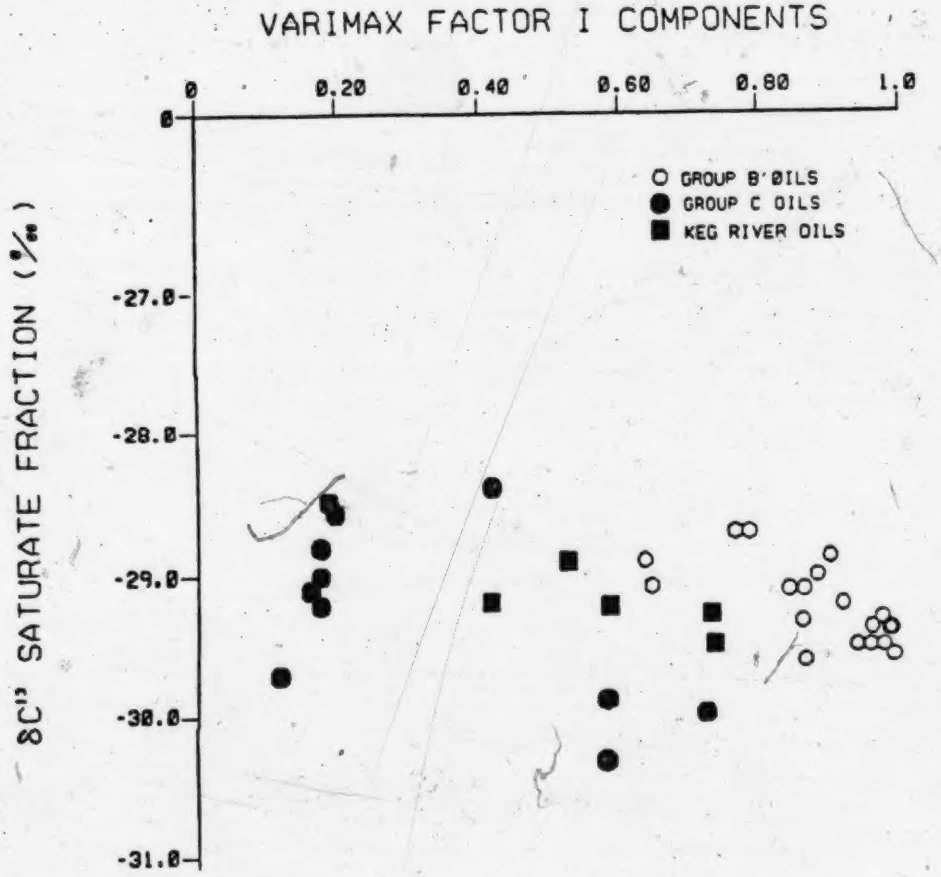


FIGURE II - 19
PLOT OF δC¹³ (AROMATIC FRACTION) vs THE VARIMAX FACTOR I COMPONENT FOR KEG RIVER AND D-3 OILS

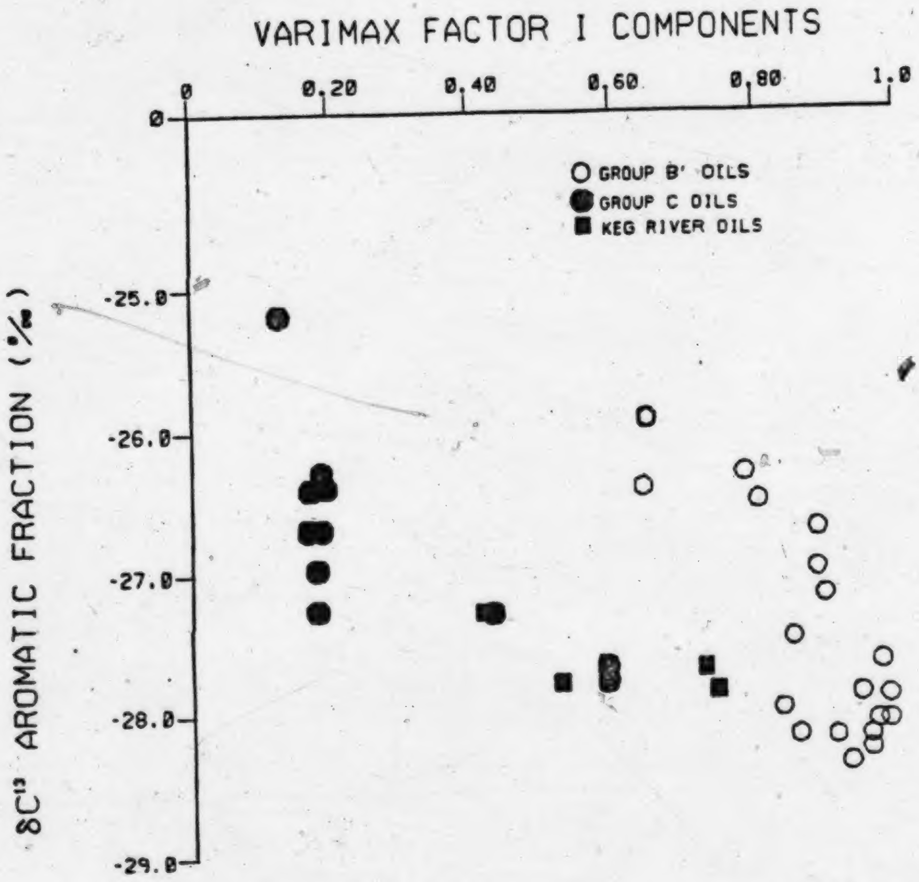
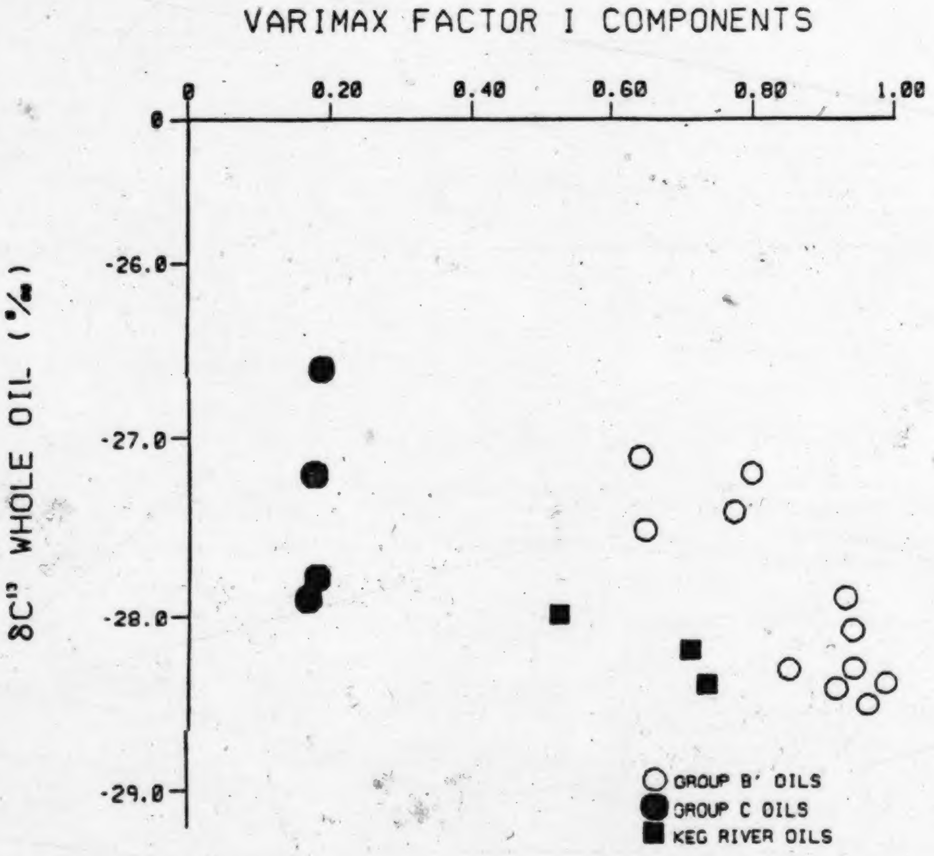


FIGURE II - 20

PLOT OF $\delta C^{13}_{\text{WHOLE OIL}}$ VS FACTOR I FOR D-3 AND KEG RIVER OILS



increasing extent of maturation which supports the aforementioned theoretical and experimental conclusions. Therefore, for the Group B' oils, the observed C^{12} enrichment of the whole oils with progressive maturation does not conform to the accepted trend (C^{13} enrichment). A C^{12} enrichment of an oil could be achieved if appreciable methane was not produced during maturation (and therefore C^{12} retained in the oil) and the isotopically heavy condensed cyclic products, or a portion of them, precipitated within the reservoir by a process such as gas deasphalting. The decline of the maltene content of the D-3 oils with increasing initial gas to oil ratio (GOR) values supports the gas deasphalting process (see Figure II - 21). In Figure II - 22 the δC^{13} values of the whole oil have been plotted against initial GOR values. The observed δC^{12} enrichment in the oils with increasing solution gas content, for the Group B' crudes, suggests that gas deasphalting could produce the positive correlation between C^{12} content and maturation by the precipitation of the C^{13} - enriched complex residue. Implicit in this argument is a positive correlation between GOR and maturation. This correlation although valid (see Figure II - 23) is probably indirect and related not to gas production by the maturation of pooled hydrocarbons but to gas production from the maturation of the source rocks and subsequent up dip migration. The magnitude of the initial GOR is therefore related to the proximity of an oil pool to the metamorphosed source rocks. This type of argument is indirect and will be reviewed when the carbon isotopes of the C_1, C_2 and C_3 gases are discussed in Chapter III.

FIGURE II-21

PLOT OF INITIAL GOR vs % MALTENES

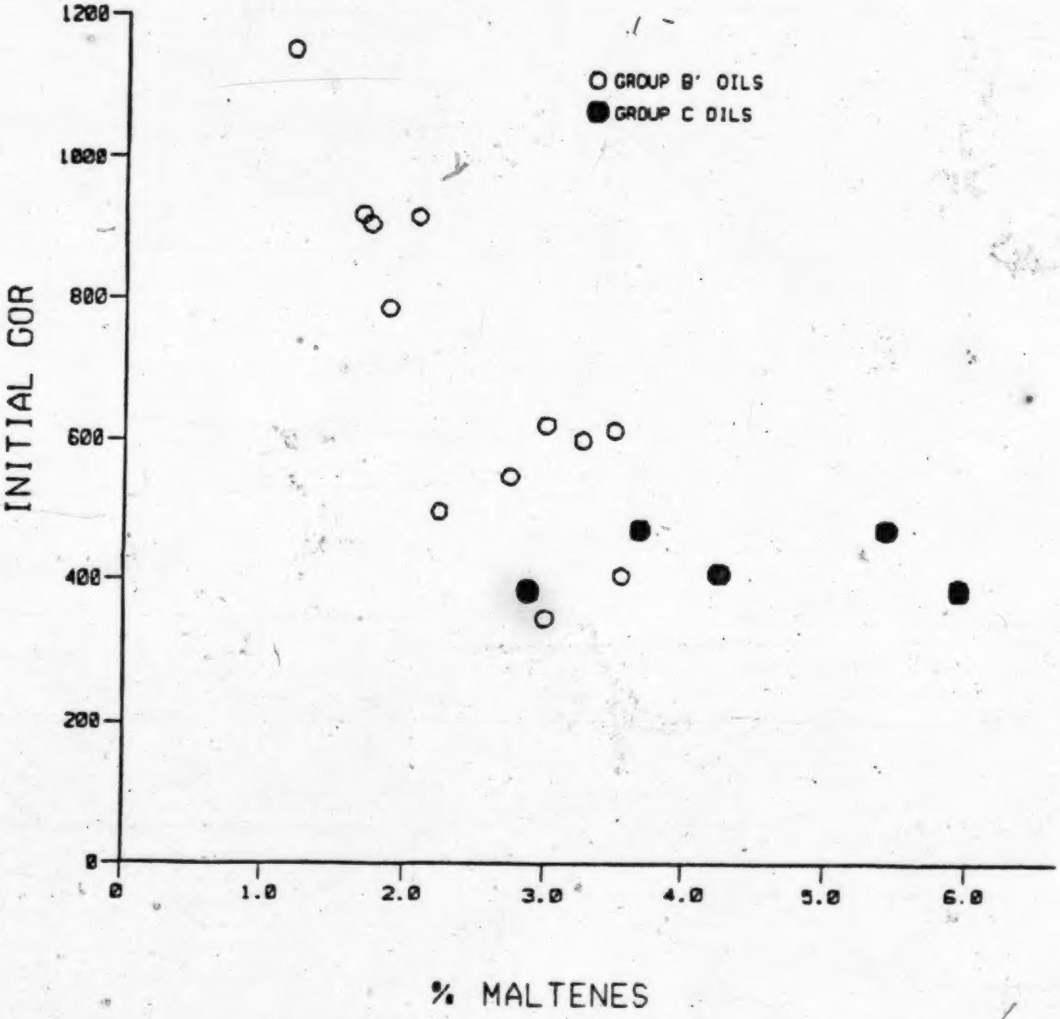
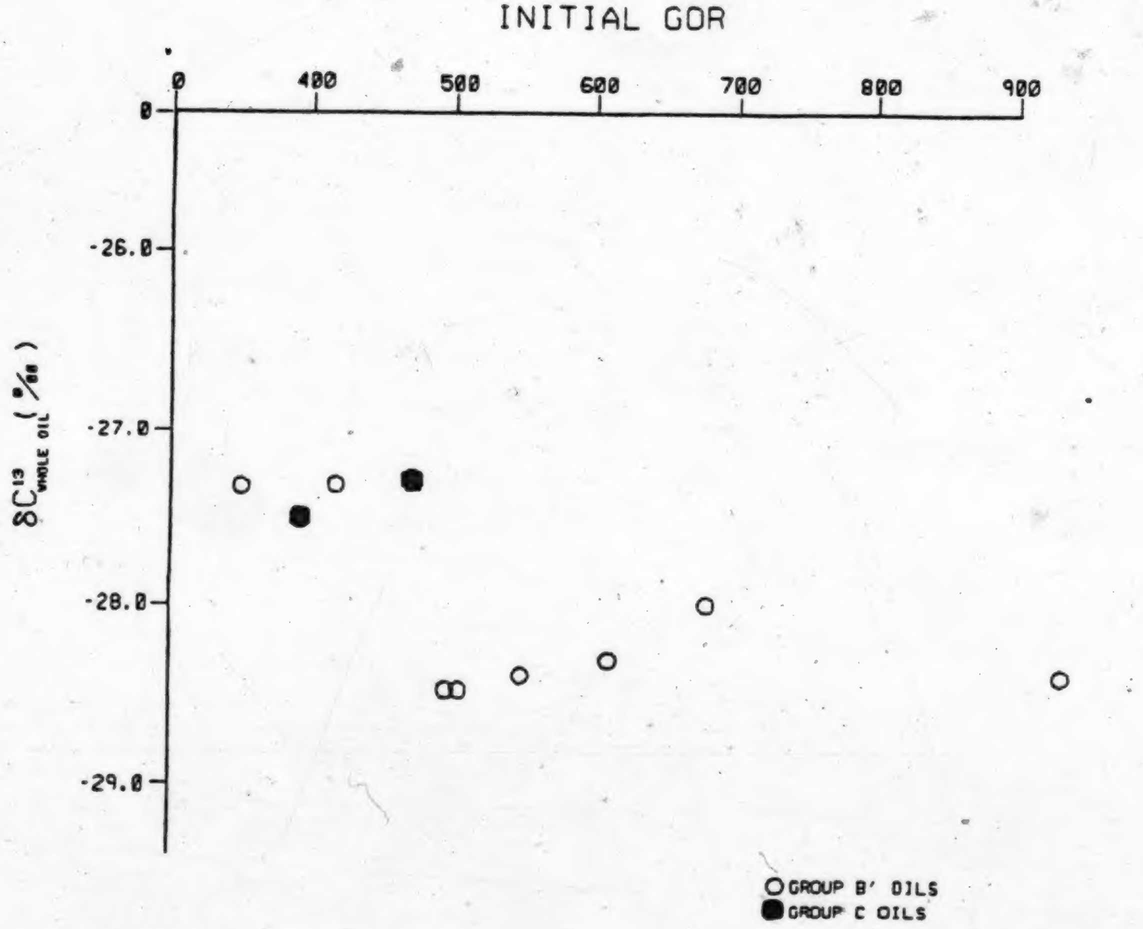


FIGURE II-22

PLOT OF δC^{13} (WHOLE OIL) vs INITIAL GOR FOR D-3 OILS



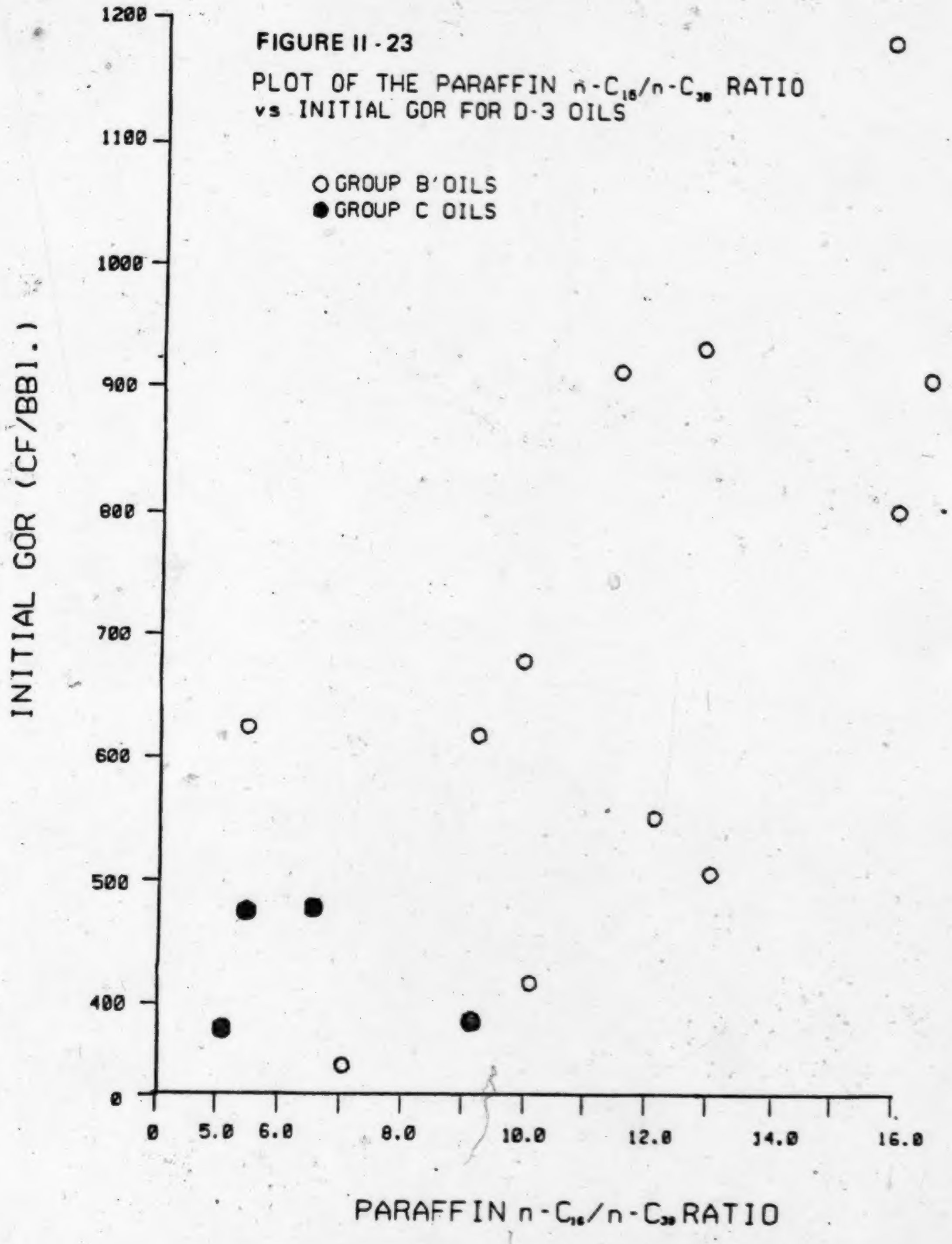


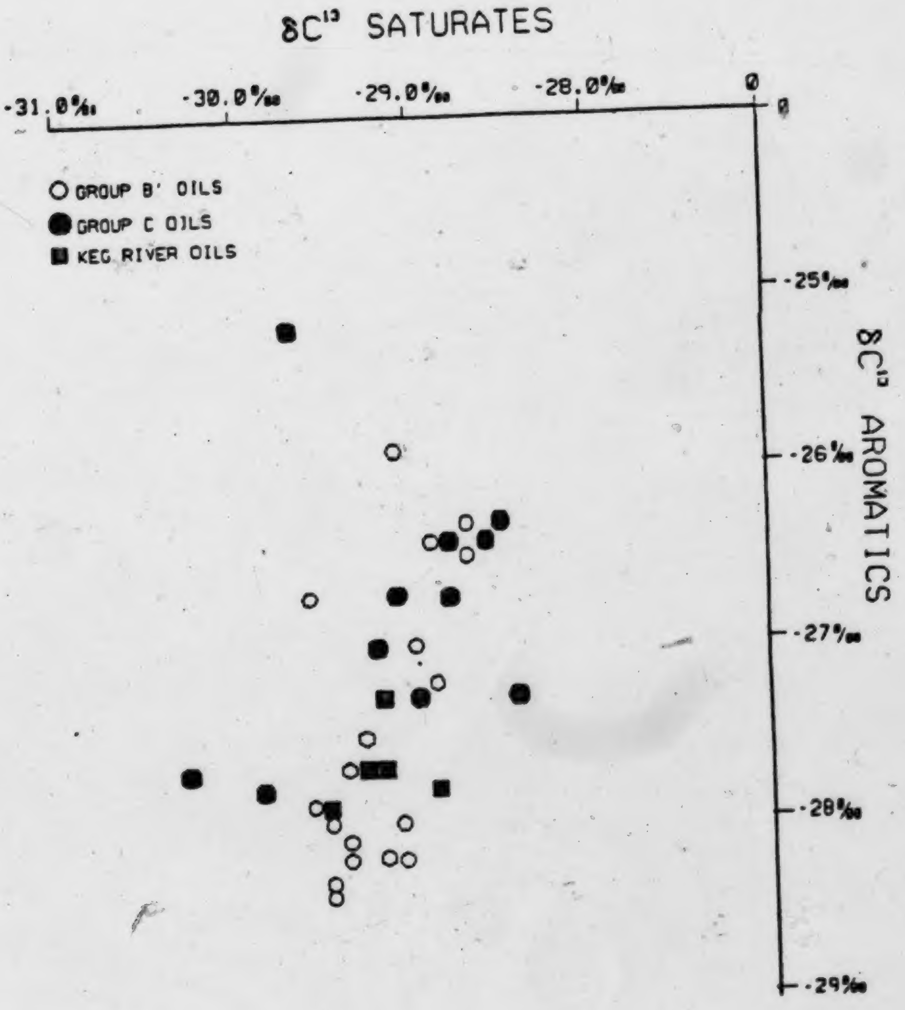
FIGURE II-23

PLOT OF THE PARAFFIN $n\text{-}C_{16}/n\text{-}C_{30}$ RATIO vs INITIAL GOR FOR D-3 OILS

The range of $_{\delta}C^{13}$ values for the whole oils (see Figure II - 16) is 1.4^{o}/oo and can be attributed to maturation. This range encompasses nearly 27% of the variation in the entire Devonian δC^{13} oil population defined by Degens (1969). Furthermore, the overlap of the δC^{13} whole oil populations for the D-3 and Keg River oils (see Figure II - 16) makes it impossible to discriminate between these oils using δC^{13} values, a correlation technique suggested by Erdman and Morris (1974). According to Koons et al. (1974) a plot of $\delta C^{13}_{\text{Aromatics}}$ vs $\delta C^{13}_{\text{Saturates}}$ can be used to discriminate between oil families. This plot (see Figure II - 24) does not distinguish between the Keg River and D-3 oils. These authors also noted that the range in δC^{13} values for the aromatic oil fraction was greater than that of the saturates. The standard deviation of δC^{13} values for the saturate and aromatic fractions for the Devonian oils studied in this thesis, respectively 0.8^{o}/oo and 0.4^{o}/oo, supports this conclusion. A comparison of the standard deviations of δC^{13} values for the whole oil (SD = 0.6), aromatic fraction (SD = 0.8) and saturate fraction (SD = 0.4) indicates that the saturate fraction data shows least variance and is therefore best suited to oil correlation problems, in agreement with Fuex (1977). However, due to the significant linear relationships between maturation and the δC^{13} values of the whole oils, and the saturate and aromatic fractions, documented in this thesis and by Koons et al. (1974), it is necessary, when correlating oils, to define an oil family (refer to Marzec et al., 1971) and its δC^{13} variation and then correlate on the

FIGURE II - 24

PLOT OF δC13 SATURATES vs δC13 AROMATICS
FOR DEVONIAN OILS



basis of the family units rather than between single oils or groups of oils whose family membership is uncertain.

CHAPTER III

STABLE ISOTOPE COMPOSITION OF D-3 NATURAL GASES

Section 1: Introduction

Natural gas samples were taken from U. Devonian Leduc Formation oil and gas pools along the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller reef trends as well as from oil pools in the M. Devonian Keg River formation at the Rainbow-Zama-Virgo field in N.W. Alberta. The gases, with the exception of the Sylvan Lake, Westerose and Wimborne samples, were dissolved in oil and recovered by expansion using the procedure outlined in Part I, Chapter I of this thesis. None of the D-3 or Keg River pools sampled along the three reef trends or at the Rainbow-Zama-Virgo field contained metamorphosed hydrocarbon assemblages (refer to Evans *et al*. 1971). Hydrocarbon accumulations at this stage of thermal alteration generally consist of dry gases with significant concentrations of hydrogen sulphide. D-3 gas pools containing mainly methane and hydrogen sulphide were sampled at Harmattan, Strachan, Ricinus, Pine Creek and Pine N.W. (see Enclosures 1a and 1b). Some miscellaneous gas samples were taken from the Rundle Formation at Harmattan, Lookout Butte and Pincher Creek, from the Halfway Sandstone at Aitken and Wildmint, from the Viking Sandstone at Giroux Lake and from the Nahanni Formation at Beaver River. Only the analyses of the Beaver River gas have been included with the D-3 and Keg River data.

Since the majority of solution gas samples taken were sour, that is contain hydrogen sulphide in amounts greater than one mole percent, the entire solution gas content of the oil sample could not be recovered and a homogeneous sample then transferred to storage bottles using a mercury piston technique. Such a transfer procedure would result in a significant loss of the hydrogen sulphide gas component by a reaction with the mercury to form metal sulphides. It is unlikely that the expansion transfer technique used recovered a sample whose major component analysis was representative of the entire solution gas. However, the isotopic composition of the methane, ethane, propane and hydrogen sulphide components would probably be representative since none of these gas components underwent a phase change during transfer. Furthermore, no part of the transfer path was narrow enough to allow molecular flow, the gas flow was turbulent and the flow path short, therefore avoiding diffusion isotope fractionation. Unfortunately the sample programme was not designed to ascertain if there was a significant (ie, greater than analytical error) isotope difference between gas that remained dissolved in the oil and gas that was released during transfer. In the majority of cases, the solution gas content of the oil was small enough to allow nearly complete transfer of the gas, or at least the taking of a homogeneous sample large enough for isotope analysis.

One potential extraction problem as yet unsolved, is the difference between the sulphur isotope value of the total gaseous sulphide recovered as a cadmium sulphide precipitate and the sulphur isotope value of the hydrogen sulphide component of the natural gas isolated using a Porapak-Q column (see Part I, Chapter I). Only three of twelve comparisons between total reactive gaseous sulphide and hydrogen sulphide sulphur isotope values (refer to Table I - I) showed differences greater than analytical error (which is ± 0.2°/oo). The mean, range and standard deviation of the 12 isotope differences are respectively: 0.3°/oo, 1.1°/oo and 0.4°/oo. In the three comparisons where there was a significant difference, the hydrogen sulphide gas component was always more S^{32} enriched. This suggests that the chromatographic separation could have caused this isotope discrepancy as well as any "natural" cause. Many researchers assume, without proof, that there is an equivalence between the total gaseous sulphide and the hydrogen sulphide component. This assumption will also be used in this thesis. However, if the observed sulphur isotope discrepancy is not due to analytical problems, then any model constructed using the assumption that the sulphur isotope composition of the total reactive gaseous sulphide is equivalent to the sulphur isotope composition of the hydrogen sulphide component will predict an improper relationship roughly 25% of the time (ie 3/12).

Sulphur isotope and carbon isotope values for total reactive gaseous sulphide, hydrogen sulphide and the methane, ethane and propane natural gas homologs are listed in Table II - XII and Table II - XVI respectively. Analytical errors and isotope correction equations are discussed in Part I, Chapters I and II. The chromatographic techniques used to isolate and prepare the gas components for isotope analysis are discussed in Part I, Chapter I of this thesis.

Section 2: Sulphur Isotope Composition of D-3 and Keg River Natural Gas and Associated Sulphur Species

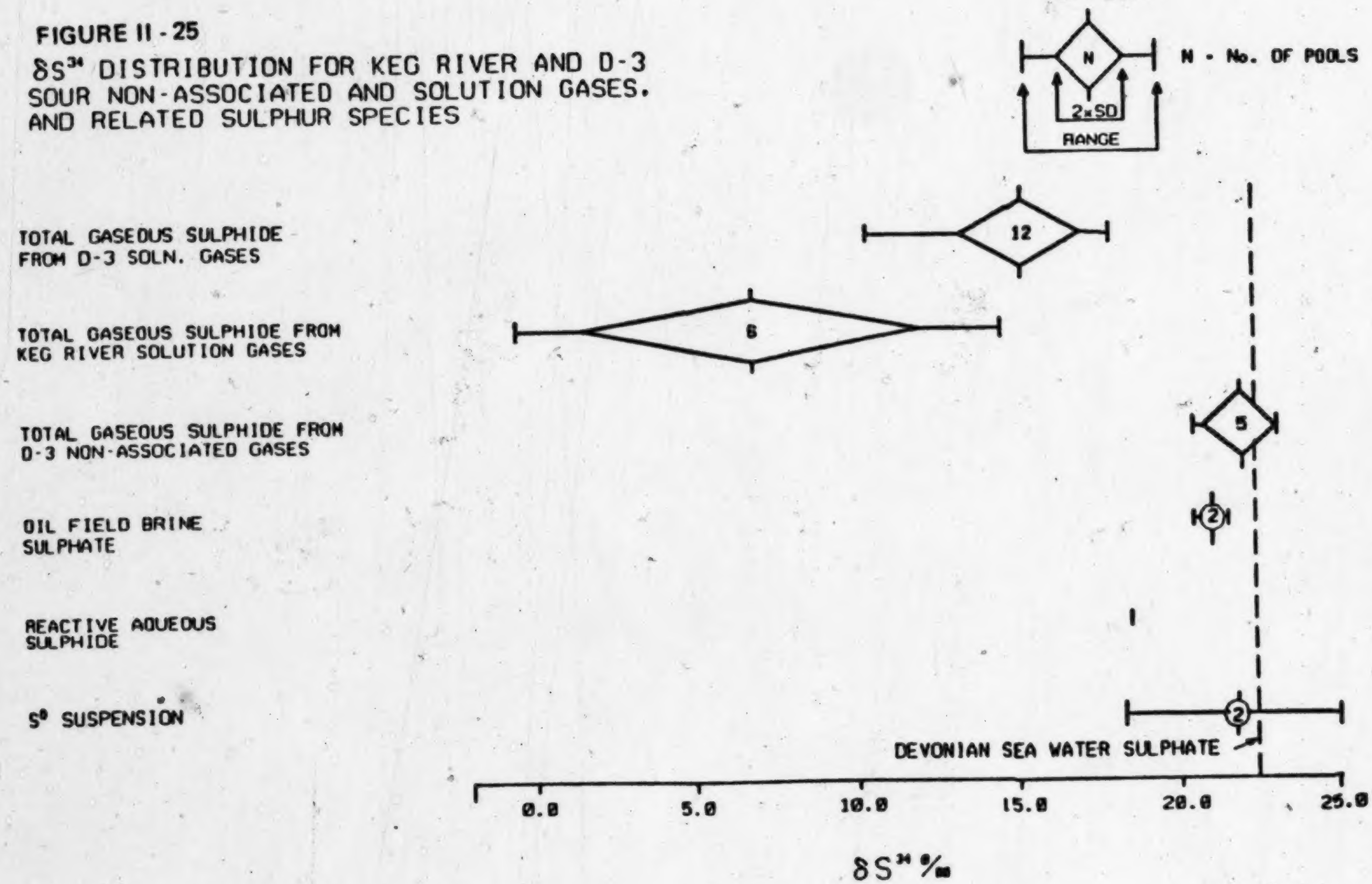
a) Sulphur Isotope Distribution for Sour D-3 and Keg River Natural Gases

The variation in sulphur isotope composition for solution gases, non-associated gases and related sulphur species from the Upper Devonian D-3 and Middle Devonian Keg River formations is illustrated in Figure II - 25. Several important facts are shown in this diagram.

First, the sulphur isotope composition of the Keg River sour solution gas is, on the average, more S^{32} enriched than the D-3 solution gas, though both sulphur isotope populations overlap to some degree. In Part II, Chapter II, the sulphur isotope composition of the Keg River oils was found to be significantly more S^{32} enriched than the D-3 oil samples. Therefore, the sulphur isotope data from both oil and solution gas samples indicates that the sulphur source for the D-3 and Keg River reservoirs is different. Furthermore, the Middle Devonian Keg River sulphur source is lighter (more S^{32} enriched) than the Upper Devonian source. If evaporite sulphate is the source of sulphur in these reservoirs, then the sulphur isotope data for the oils and gases predicts the expected trend. That is, the Middle Devonian evaporite sulphate is lighter than the Upper Devonian sulphate. Thode and Monster (1965) and Orr (personal communication, 1977) give average

FIGURE II-25

δS^{34} DISTRIBUTION FOR KEG RIVER AND D-3 SOUR NON-ASSOCIATED AND SOLUTION GASES. AND RELATED SULPHUR SPECIES



sulphur del values for Middle and Upper Devonian sulphate of +18°/oo and 25.0°/oo respectively. The difference between the mean sulphur isotope values of the D-3 and Keg River solution gases (8.4°/oo) is quite similar to the difference in mean sulphur isotope values between the Upper Devonian and Middle Devonian evaporite sulphates (7°/oo). This suggests that an intimate relationship could exist between the total reactive gaseous sulphide and evaporite sulphate.

Second, the mean sulphur isotope value of the non-associated (metamorphosed) gases (+21.9°/oo) is nearly the accepted isotope value of Devonian sea water sulphate (+22.4°/oo, see Thode and Monster, 1965). The heaviest sulphur isotope value of the non-associated gases (23.0°/oo) is 0.6°/oo heavier than the Devonian sea water sulphate del value and only 2.0°/oo lighter than the mean Upper Devonian reservoir sulphate value (Av. δS^{34} = +25.0°/oo). If evaporite sulphate is the source for natural gas hydrogen sulphide, then the hydrogen sulphide from the metamorphosed natural gas appears to be derived from sulphate through a chemical reaction that involves little or no sulphur isotope fractionation (see Orr, 1974). Alternatively, the metamorphosed D-3 reservoirs could act as closed chemical systems and the trapped hydrogen sulphide could then represent a gas accumulation from the near complete reduction of the source sulphate supply. In this alternate case, a large sulphur isotope fractionation factor could be involved in the sulphate reduction reaction. However, the magnitude of this fractionation factor can be determined directly from the measurement of the sulphur isotope composition of the hydrogen sulphide gas only during the very initial stages of sulphate reduction (Kemp and Thode, 1968).

The mean sulphur del value of the Upper Devonian oil field brine sulphate (+21.4^{0}/oo)* indicates that these sulphates have probably been derived from Upper Devonian evaporites (Av. S^{34} = +25.0^{0}/oo) within the Leduc reservoir system.

Two samples of coexisting reactive gaseous sulphide and elemental sulphur (S_8), suspended in coproduced oilfield brine, were obtained from D-3 reservoirs. The difference in the measured sulphur isotope composition of the elemental sulphur suspension and reactive gaseous sulphide was 0.8^{0}/oo for the Sylvan Lake sample and 2.8^{0}/oo for the Pine Creek sample (See Table II - XII). Tudge and Thode (1950) calculated the equilibrium isotope fractionation between hydrogen sulphide and elemental sulphur (S_8) to be 3.0^{0}/oo at both 0°C and 25°C. The elemental sulphur was enriched in the heavier isotope. The gas and sulphur samples collected for this thesis were separated for isotope analysis at room temperature (22°C). Since the sulphur isotope value of the Pine Creek elemental sulphur (+25.0^{0}/oo) is 2.8 per mil heavier

---

*Thode and Monster (1965) noted that brine sulphate could be 1.6^{0}/oo lighter than coexisting crystalline gypsum.

TABLE II - XII

Sulphur Isotope$^+$ Values for Albertan Devonian Oils, Sour Non-Associated and Solution Gases, and Related Aqueous Sulphides and Brine Sulphates

Pool Name		Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Big Lake	D-3	13-25-53-26W4	+15.0	+14.4				
		9-26-53-26W4	+15.0	+13.6				
Acheson	D-3	4-10-52-26W4	+12.3					
Yekau Lake	D-3	8-4-52-26W4	+12.5					
Leduc Woodbend	D-3	13-3-50-26W4	+13.1					
		8-5-51-26W4	+13.2					
		8-9-50-26W4	+13.1					
Golden Spike	D-3	10-27-51-27W4	+15.2					
		12-26-51-27W4	+15.2					
Wizard Lake	D-3	1-21-48-27W4	+16.0					
Glen Park	D-3	4-2-49-27W4	+13.8					
		5-2-49-27W4	+13.1					

All δS^{34} values are given in reference to the Canyon Troilite Standard.

TABLE II - XII (Cont'd)

Pool Name	Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Bonnie Glen	D-3 14-6-47-27W4	+14.9					
Sylvan Lake	D-3 Separator Sample	+18.1	+17.5		+18.5	+18.3	+21.8
Westerose	D-3 Battery Sample	+15.0	+17.7				
			+17.7				
			+17.9				
West Drumheller	D-3 11-1-30-21W4	+5.5	+10.2				
	12-1-30-21W4	+5.6	+10.5				
New Norway	D-3 11-36-44-22W4	+10.2	+13.6				
Buffalo Lake	D-3 4-35-39-21W4	+17.2	+15.4	+14.7			
Bashaw	D-3 10-6-42-22W4	+14.5	+15.8	+14.7			
Erskine	D-3 2-7-39-20W4	+17.4	+15.4				
	6-19-39-20W4	+17.0	+15.2				
	8-13-39-21W4	+17.1					+21.0
	8-26-39-21W4	+16.5	+15.2	+15.1			
Stettler	D-3 12-3-38-20W4	11.9	14.5				
	16-9-38-20W4	11.9	14.4				
	16-16-38-20W4	12.6	14.4				

TABLE XII (Cont'd)

Pool Name		Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Malmo	D-3	5-14-44-22W4	+8.9	+16.0				
		2-23-44-22W4	+8.7	+15.7				
Clive	D-3A	16-29-40-24W4	+9.9	+15.8				
		12-33-40-24W4	+10.1	+15.5	+15.5			
Wimborne	D-3	4-1-33-26W4		+16.3				
		6-11-33-26W4	+18.9					
		7-26-33-26W4		+16.4	+16.3			
Zama Keg River		6-23-116-4W6	+0.9					
		7-7-116-5W6	+0.2	+5.5				
		4-36-116-6W6	-2.5	+10.4				
		12-21-117-4W6	-1.3	+5.1				
		2-25-117-5W6	+0.2	-0.5				
Virgo Keg River		4-6-115-5W6	-0.3	+5.5				
		5-11-115-5W6	+2.3					
		5-27-115-5W6	+2.5	+14.6				
Rainbow Keg River		8-32-111-7W6	+6.8					
Non-Associated Gases								
Ricinus	D-3	7-13-36-10W5		+20.4	+20.4			
		10-33-36-10W5		+20.5				

TABLE II - XII (Cont'd)

Pool Name	Well Location	δS^{34} Oil	δS^{34} Gaseous Total Sulphide	δS^{34} Gas H_2S only	δS^{34} Reactive Aqueous Sulphide	δS^{34} S° Suspension	δS^{34} Brine Sulphate
Non Associated Gases - Cont'd							
Strachan	D-3 10-31		+20.6				
	7-32		+20.7				
Harmatten E.	D-3 #1		+23.0				
	#2		+22.6	+22.4			
Pine Creek	D-3 10-16		+22.2			+25.0	
	10-23		+22.7	+22.0			
Pine N. W.			+23.0				

(more S^{34} enriched) than the associated reactive sulphide* (+22.2^{0}/oo) it is possible that these two sulphur phases are in equilibrium both in the sample bomb and in the reservoir. For the Sylvan Lake sample, the much smaller isotope difference (+0.8^{0}/oo) between elemental sulphur (δS^{34} = +18.3^{0}/oo) and coexisting reactive gaseous sulphide (δS^{34} = +17.5^{0}/oo) may represent equilibrium fractionation that was established at reservoir temperature (79°C) and then maintained. At any rate, both the magnitude and direction of sulphur isotope enrichment in the two D-3 sulphur samples is compatible with an equilibrium isotope exchange reaction between hydrogen sulphide and elemental sulphur (S_8).

b) Temperature Dependence of the Sulphur Isotope Composition of Sour Natural Gases - The Closed System Model

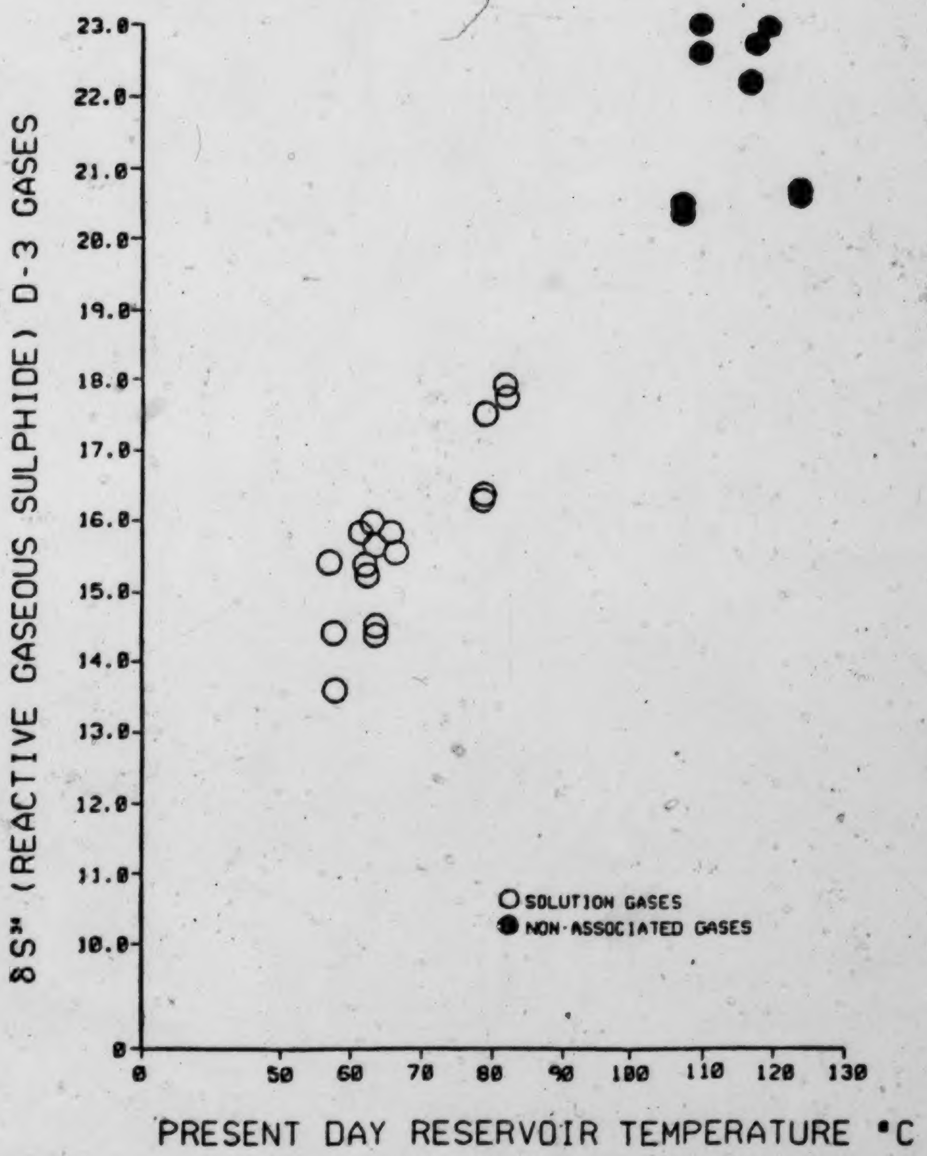
In Figure II - 26 the sulphur isotope composition of the reactive gaseous sulphide (RGS) has been plotted versus present day reservoir temperature. The correlation coefficient (r) for this plot is 0.954. Therefore, the hypothesis that the sulphur del value of the RGS is independent of present day reservoir temerature can be rejected at the

---

*The chromatographed hydrogen sulphide component of the Pine Creek gas has a del value of +22.0^{0}/oo.

FIGURE II-26

PLOT OF δS³⁴ OF THE TOTAL GASEOUS SULPHIDE
vs PRESENT DAY RESERVOIR TEMPERATURE
FOR D-3 POOLS



5% level of significance. The correlation equation of present day reservoir temperature versus δS^{34}_{RGS} is:

$$\text{TEMP. } (^\circ C) = 7.34\ \delta S^{34}_{RGS} - 46.79$$

The standard error for the estimated temperature is 7°C.

It is possible to construct a chemical model which can be fit, with some degree of success, to the sulphur isotope composition of the reactive gaseous sulphide and present day reservoir temperature data. In this model reservoir sulphate (anhydrite) is reduced to hydrogen sulphide through Toland (1960) reactions which function in a closed chemical system. The chemical reactions were assumed to be one way, first order kinetic, and the sulphur isotope fractionation factor involved was chosen as a constant whose value is 1.022 in agreement with work published by Harrison and Thode (1957) and Husain (1967). The sulphur isotope composition of D-3 reservoir sulphate was selected to be +25^{0}/oo from data collected by Orr (personal communication, 1977). Before critically evaluating this model it is necessary to develop it mathematically and point out its utility.

The mathematics of the closed system model were developed by Rayleigh (1896). Once any chemical system becomes closed, no reactants or products may enter or leave. The system is self contained. As a result the fraction of reactant converted to product can be calculated from the initial isotope composition of the reactant and the isotope composition of the remaining reactant or accumulated product at some point in the reaction. For an irreversible first order kinetic reduction reaction such as R → P, a rate constant K can be defined. Let the amount of the reactant (R) and product (P) containing the most abundant isotope be respectively R' and P'. And, let the amount of reactant (R) and product (P) containing the least abundant isotope be respectively R" and P". Due to the mass differences between the two isotopes, the molecular species containing the two isotopes will have different vibrational frequencies, and rotational and translational motions. As a result the rates of reduction (characterized by K) will be different for R' and R". If R' represents the concentration of the light isotope and R" represents the concentration of the heavy isotope, then K' is greater than K". According to Harrison and Thode (1957) the ratio of the rate constants (K'/K") can be equated to the isotope fractionation factor (see also Bigeleisen, 1949). From the two isotopic reactions:

$$R' \xrightarrow{K'} P'$$

$$R'' \xrightarrow{K''} P''$$

the following rate equations can be written:

$$+\frac{dP'}{dt} = K'R'$$

$$+\frac{dP''}{dt} = K''R''$$

It follows that:

$$\frac{dP'}{dP''} = \frac{K'}{K''}\frac{R'}{R''} \qquad \text{II - 10}$$

The concentration of the remaining reactant (R) can be expressed in terms of the initial concentration of the reactant (Ro) and the product (P). That is, R = Ro - P. Substituting this expression into equation II - 10, it can be rewritten as:

$$\frac{dP'}{dP''} = \frac{K'}{K''}\frac{Ro' - P'}{Ro'' - P''}$$

Since $\frac{K'}{K''} = \alpha$, then $\frac{dP'}{dP''} = \alpha \frac{(Ro' - P')}{(Ro'' - P'')}$

Also, $\frac{dP'}{Ro' - P'} = \alpha \frac{dP''}{(Ro'' - P'')}$

II - 11

Let u' = Ro' - P' and u" = Ro" - p"

Therefore, du' = - dP' and du" = - dP"

Therefore, $-\frac{du'}{u} = \alpha - \frac{du''}{u''}$

Expressing this in integral form:

$$\int \frac{du'}{u'} = \alpha \int \frac{du''}{u''}$$

$$\ln u' + C' = \alpha(\ln u'' + C'')$$

The constants can be evaluated at $\ln u + C = 0$

$$\ln u' - \ln u'_0 = \quad (\ln u'' - \ln u''_0) \qquad \text{II - 12}$$

Making the substitutions outlined in equation II - 11, equation II - 12 becomes $\ln (Ro' - P') - \ln (Ro' - Po') = \alpha[(\ln Ro''-P'')-\ln(Ro''-Po'')]$

Since $Po' = 0$ and $Po'' = 0$

Then, $\ln (Ro' - P') - \ln Ro' = \alpha[\ln(Ro''-P'') - \ln Ro'']$

Also, $\ln \frac{Ro' - P'}{Ro'} = \alpha \ln \frac{Ro'' - P''}{Ro''}$

Simplifying further: $\frac{1}{\alpha} \ln(1 - \frac{P'}{Ro'}) = \ln(1 - \frac{P''}{Ro''})$

Subtracting $\ln \frac{P'}{Ro'}$ from each side:

$$\frac{1}{\alpha} \ln \left(1 - \frac{P'}{Ro'}\right) - \ln \frac{P'}{Ro'} = \ln \left(\frac{1}{\frac{P'}{Ro'}} - \frac{\frac{P''}{Ro''}}{\frac{P'}{Ro'}}\right)$$

Since P' and Ro' represent the most abundant isotope then the ratio $\frac{P'}{Ro'}$ approximates to a good degree the fraction of reactant converted to product.

Let $\frac{P'}{Ro'} = f$

Therefore $\frac{1}{\alpha} \ln (1 - f) \; - \ln f = \ln (\frac{1}{f} - \frac{P''/P')}{Ro''/Ro'}$ II - 13

The expression $\frac{P''/P'}{Ro''/Ro'}$ can be expressed in terms of the δ notation. δ is defined as:

$$\delta_{A-B} = (R_A/R_B - 1)\ 1000 \text{ (see Bottinga, 1969)}$$

Where δ_{A-B} is the isotope composition of substance A with respect to substance B and R_A and R_B are the isotope ratios of substances A and B.

Also, $R_A/R_B = \alpha$ and $\Delta = 1000(\alpha - 1)$ (Bottinga, 1969). Therefore,

$$\Delta = 1000 \left(\frac{R_A}{R_B} - 1\right)$$

As a result, $\Delta = \delta_{A-B}$

The expression $\frac{P''/P'}{Ro''/Ro'}$, in equation II - 13, can be written as:

$$1 + \left(\frac{R_P}{R_{Ro}} - 1\right) \frac{1000}{1000}$$

In view of the preceding discussion:

$$\frac{P''/P'}{Ro''/Ro'} = 1 + \delta_{P-Ro}/1000 \qquad \text{II - 14}$$

Also, $\frac{P''/P'}{Ro''/Ro'} = 1 + \frac{\Delta}{1000}$ II - 15

Substituting for $\frac{P''/P'}{Ro''/Ro'}$, equation II - 13 becomes:

$$\frac{1}{\alpha}\ln(1-f) - \ln f = \ln\left(\frac{1}{f} - 1 - \frac{\Delta}{1000}\right)$$

Therefore $\frac{1}{\alpha}\ln(1-f) - \ln f = \ln\frac{1-f}{f} - \frac{\Delta}{1000}$

This expression can be simplified further to:

$$\Delta = -1000\left(\frac{1-f}{f}\right)\left[(1-f)^{\frac{1}{\alpha}-1} - 1\right] \qquad \text{II - 16}$$

The relationship between the fraction of reactant converted to product and temperature can be derived from the first order rate equation.

$$-\frac{dR'}{dt} = K'R'$$

Rearranging: $-\frac{dR'}{R'} = K'dt$

Integrating this expression:

$$\int_{Ro'}^{R}\frac{dR'}{R} = K'\int_{to}^{t} dt$$

Therefore $-\ln\frac{R'}{Ro'} = K't$

Since $\frac{R'}{Ro'} = 1-f$

$-\ln(1-f) = K't$

Therefore $\frac{1}{1-f} = e^{K't}$ or, $f = 1-e^{-K't}$ II - 17

According to Arrhenius theory, the rate constant (K) is a function of the pre-exponential factor (A), the activation energy (Ea) and the absolute temperature (T). More precisely: $K=Ae^{-Ea/Rt}$ Where R is the ideal gas constant whose value is 1.9872 cal/degree mole. Substituting this expression for K into equation II - 17 gives:

Therefore:

$$\Delta = -1000 \frac{e^{-tAe^{-Ea/RT}}}{1-e^{-tAe^{-Ea/RT}}} \left(e^{-\frac{tA}{\alpha} e^{-Ea/RT} + tAe^{-Ea/RT}} - 1\right)$$

This simplifies to:

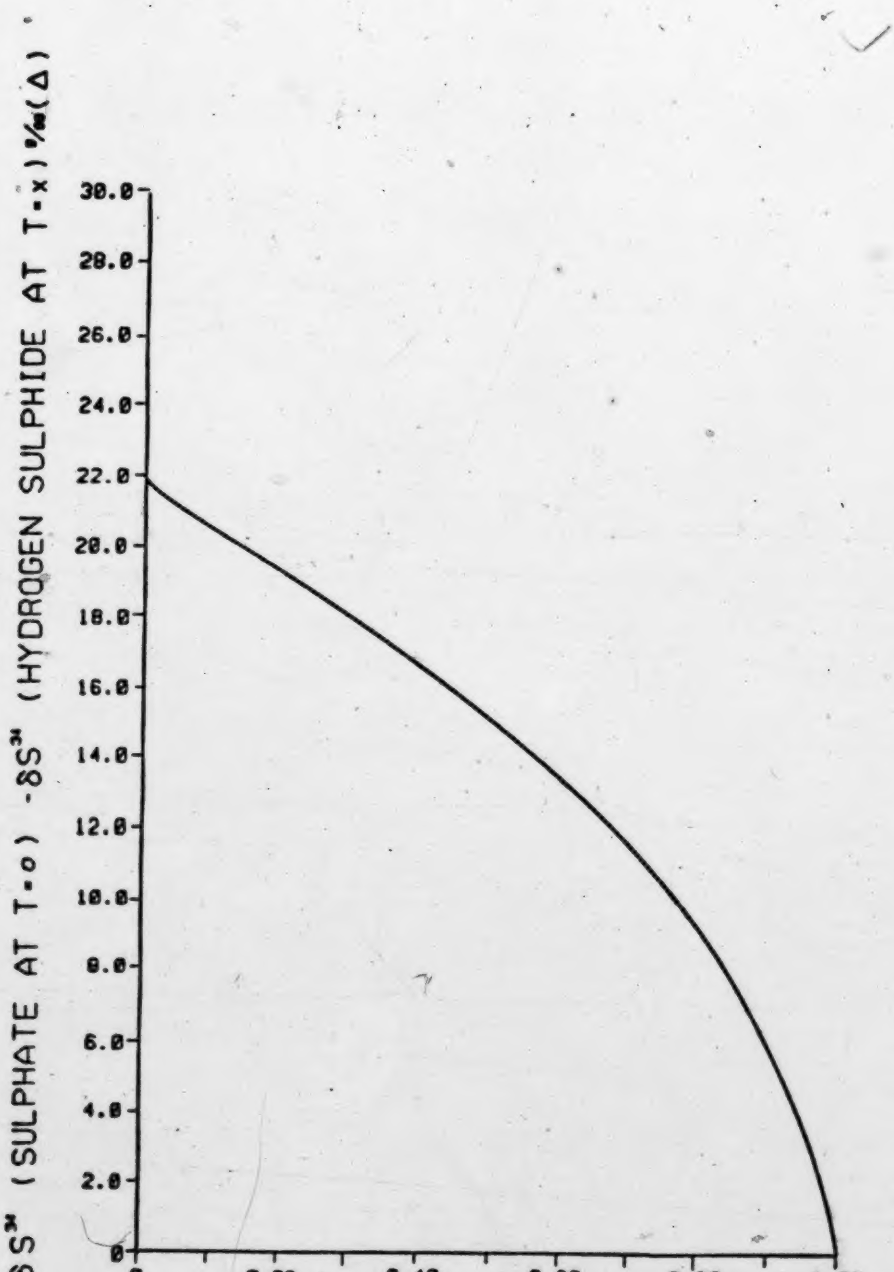
$$\Delta = \frac{-1000}{1-e^{-tAe^{-Ea/RT}}} \left(e^{-\frac{tA}{\alpha} e^{-Ea/RT}} - e^{-Ate^{-Ea/RT}}\right) \qquad \text{II - 18}$$

Equation II - 18 can be stated in terms of the sulphur isotope composition of hydrogen sulphide in the reservoir system. The difference (Δ) between the isotope composition of the cumulative hydrogen sulphide (product) and the initial isotope composition of the sulphate (reactant) is dependent on the fraction (f) of sulphate reduced to hydrogen sulphide which is in turn dependent on time (t) and absolute temperature (T). Ea, A and α are constants and have values specified by the rate controlling step. Therefore, for a series of contemporaneous closed sulphur systems that are closely associated with progressively deeper (hotter) hydrocarbon accumulations, the isotope composition of hydrogen sulphide will be a function of reservoir temperature.

In Figure II - 27 the sulphur isotope difference (Δ) between hydrogen sulphide and initial sulphate has been plotted versus the fraction of sulphate converted to hydrogen sulphide (f). This plot shows that as f approaches 1, the sulphur isotope composition of hydrogen sulphide approaches the initial isotope composition of sulphate. And, where f approaches zero, the sulphur isotope composition of hydrogen sulphide approaches the value 1000 (α - 1). If α is specified as 1.022 and the initial sulphur isotope composition of sulphate is +25^{o}/oo, then the del value of hydrogen sulphide should range from +25^{o}/oo to +3^{o}/oo, referred to Canyon Diablo troilite. This range includes the D-3 sour gas sulphur isotope date (see Figure II - 25). Equation II - 18 also indicates that no correlation need occur between the sulphur isotope composition of hydrogen sulphide and its mole percent or between mole percent hydrogen sulphide and reservoir temperature. This results from the fact that these variables correlate with the fraction of reservoir sulphate reduced to hydrogen sulphide. Therefore, for pools with relatively small amounts of initial reservoir sulphate, relatively small volumes of hydrogen sulphide will occur in the gas cap regardless of reservoir temperature. However, the general statement that the most likely place to find large concentrations of hydrogen sulphide is in deeper hotter pools is valid since these pools would have the greatest amount of sulphate reduced to hydrogen sulphide. In Figures II - 28 and II - 29 the poor correlation between mole percent hydrogen sulphide and reservoir temperature, and mole percent hydrogen sulphide and its sulphur isotope composition is apparent (see also Krouse, 1977).

FIGURE II - 27

PLOT OF Δ vs f FOR α = 1.022



FRACTION OF COMPLETION OF REACTION (f)

FIGURE II-28

PLOT OF MOLE PERCENT HYDROGEN SULPHIDE VERSUS PRESENT DAY RESERVOIR TEMPERATURE FOR D-3 POOLS

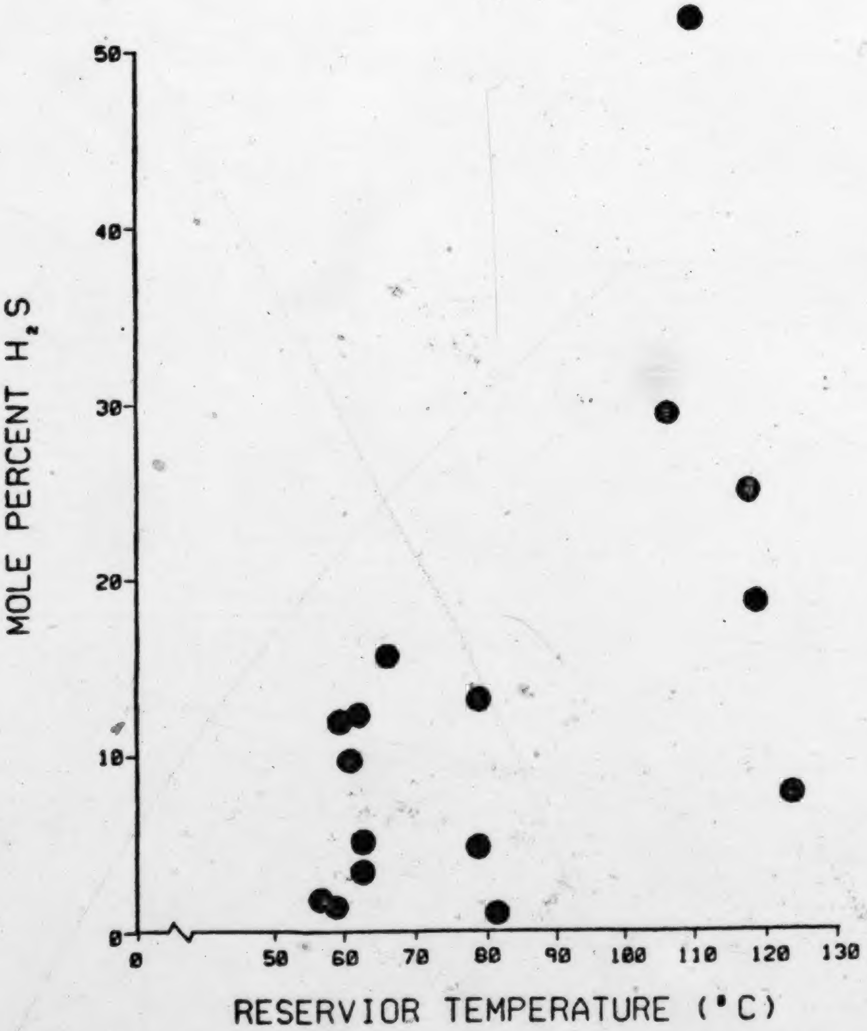
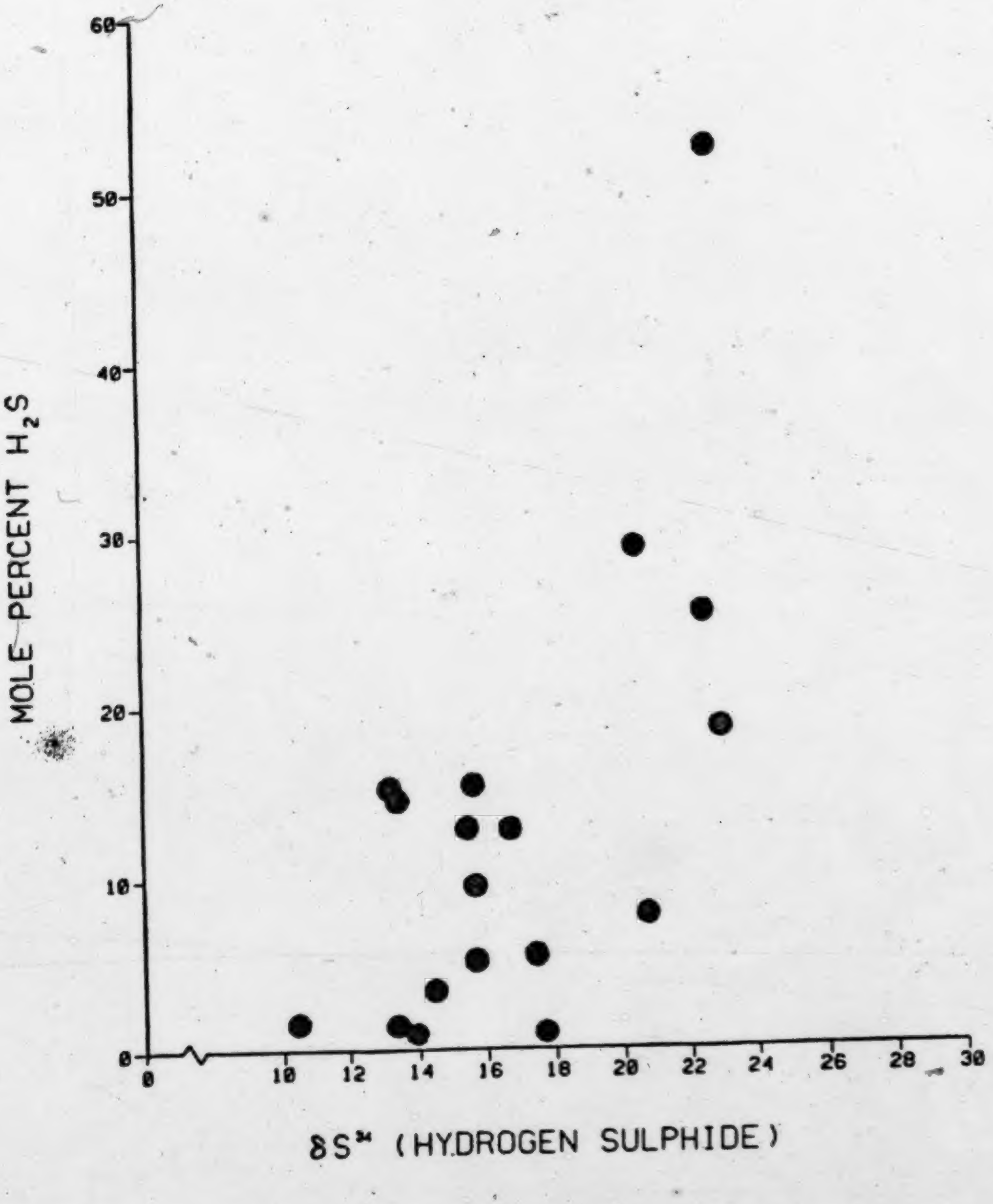


FIGURE II - 29

PLOT OF MOLE PERCENT HYDROGEN SULPHIDE VERSUS δS^{34} (HYDROGEN SULPHIDE) FOR D-3 POOLS



Since no values for Ea and A are known for the reduction of sulphate to hydrogen sulphide in the hydrocarbon system, these can be estimated from the sulphur isotope composition of RGS and reservoir temperature data. Two linear simultaneous equations of the form:

$$\ln A - \frac{Ea}{RT_1} = \ln K_1$$

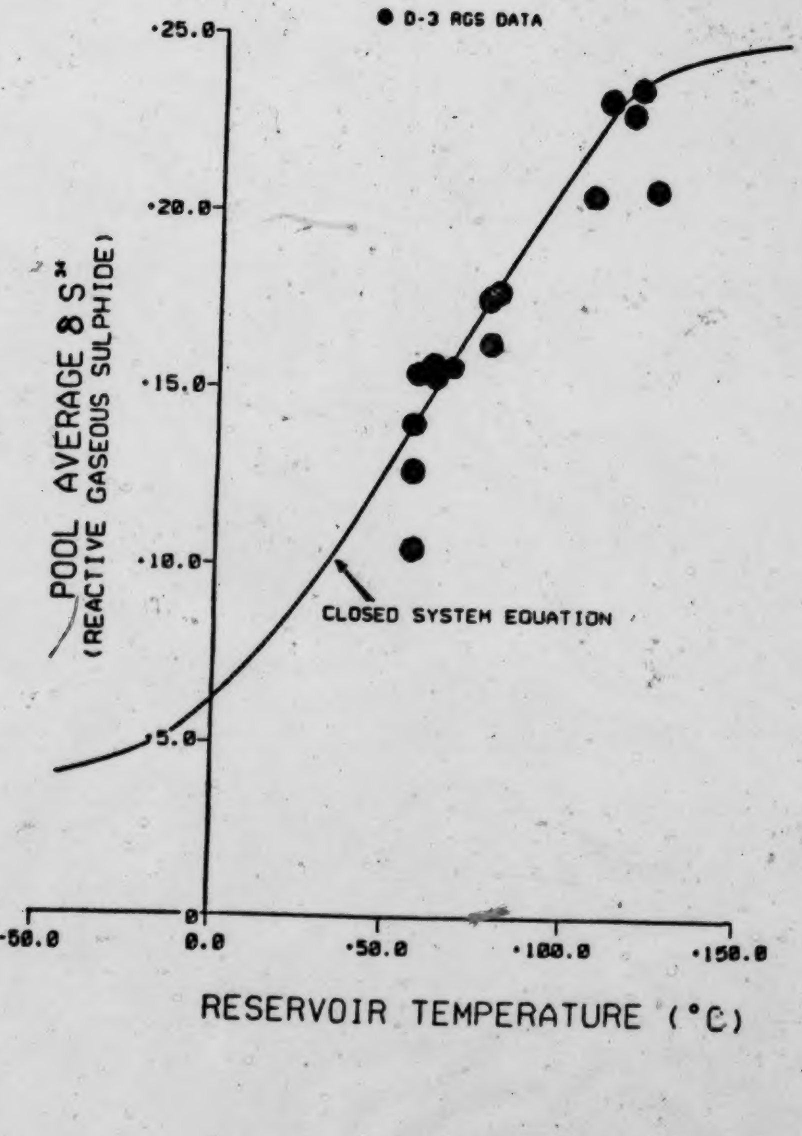
$$\ln A - \frac{Ea}{RT_2} = \ln K_2$$

can be solved. K can be evaluated through the following relationship: $K = \frac{-\ln(1 - f)}{t}$, where f is the fraction of sulphate reduced to hydrogen sulphide and t is the length of time (seconds) taken by the chemical reaction to achieve a given extent of completion (f). F is related to the sulphur isotope difference between initial sulphate and H_2S product (Δ) through equation II - 16. Using the following values: $\alpha = 1.022$; $t = 2.0512 \times 10^{15}$ secs (65 myrs); $T_1 = 305.9°K$; $T_2 = 315.5°K$; $\Delta_1 = 15.03$; $\Delta_2 = 13.28$; Ea and A were determined to be: 4.85 K cal and 9.782×10^{-13} respectively. Ea and A were calculated in order that equation II - 18 could be plotted. No firm chemical interpretation should be made, regarding the sulphate reduction process, based on these values of Ea and A. The applicability of the closed system model to the D-3 reservoir is simply not known. If the closed system model did apply, then the values for Ea and A would represent only average values whose relationship to the actual values are uncertain as a result of fluctuations in reservoir temperature over geologic time (refer to Deroo et al. 1977). If the calculated values are representative of the correct values for Ea and A, for the reduction of sulphate to hydrogen sulphide, then the energy of activation is low but the entropy of activation (which is a function of A) is so low that the reduction process is quite slow. A low energy of activation, which favors a rapid chemical reaction, coupled with an unfavorable entropy for the activated complex, which retards the chemical reaction, is usually characteristic of stearic hindrance, not uncommon in organic reactions.

In Figure II - 30 equation II - 18 has been plotted using the calculated values for Ea and A. The D-3 reactive gaseous sulphide data have been plotted for reference. Equation II - 18 plots an elongated S shape with its linear portion passing through the D-3 RGS point scatter. An attempt was made to obtain the best fit of equation II - 18 to the D-3 RGS sulphur isotope and reservoir temperature data using the Bio-Med nonlinear least squares computer program BMD07R. The program did not converge. However the linear term representating the initial sulphur isotope composition of reservoir sulphate remained constant at +25°/oo. The program did not converge probably because there was no data over the curved portion of equation II - 18 (see Figure II - 30). During fitting, small variations in the initial sulphur isotope composition of reservoir sulphate caused the nonlinear portions of the closed system curve to pass into the linear data field, and as a result the mean square deviation of the data from the best fit

FIGURE II - 30

COMPARISON OF D-3 RGS SULPHUR ISOTOPE AND RESERVOIR TEMPERATURE DATA TO THE CLOSED SYSTEM RELATIONSHIP



curve increased markedly. Therefore, the program could decide on a best fit value for the initial sulphur isotope composition of reservoir sulphate quite quickly. However, once the best fit curve was positioned within the linear data field, no further reduction in the mean square deviation could be achieved by varying Ea, A, t or T. This conclusion is easily demonstrated for the reservoir temperature variable. A series of δS^{34} (RGS) vs (Present Day Reservoir Temperature + ΔT) data were fit with a linear equation of the form $Y = mx + b$. ΔT was varied from 0 to 50°C at 10°C intervals. No variation in the mean square deviation of the δS^{34} (RGS) variable, outside of analytical error ($\pm 0.2^o$/oo), was observed (see Table II - XIII).

TABLE II - XIII

Mean Square Deviations for δS^{34} (RGS)

ΔT	Mean Square Deviation (δS^{34} vs. 1/T °K)
0	0.9075^o/oo
10	0.9095^o/oo
20	0.9081^o/oo
30	0.9076^o/oo
40	0.9114^o/oo
50	0.9065^o/oo

From Figure II - 30 it can only be concluded that the closed system model is capable of explaining the observed linear relationship between the sulphur isotope composition of the reactive gaseous sulphide and reservoir temperature.

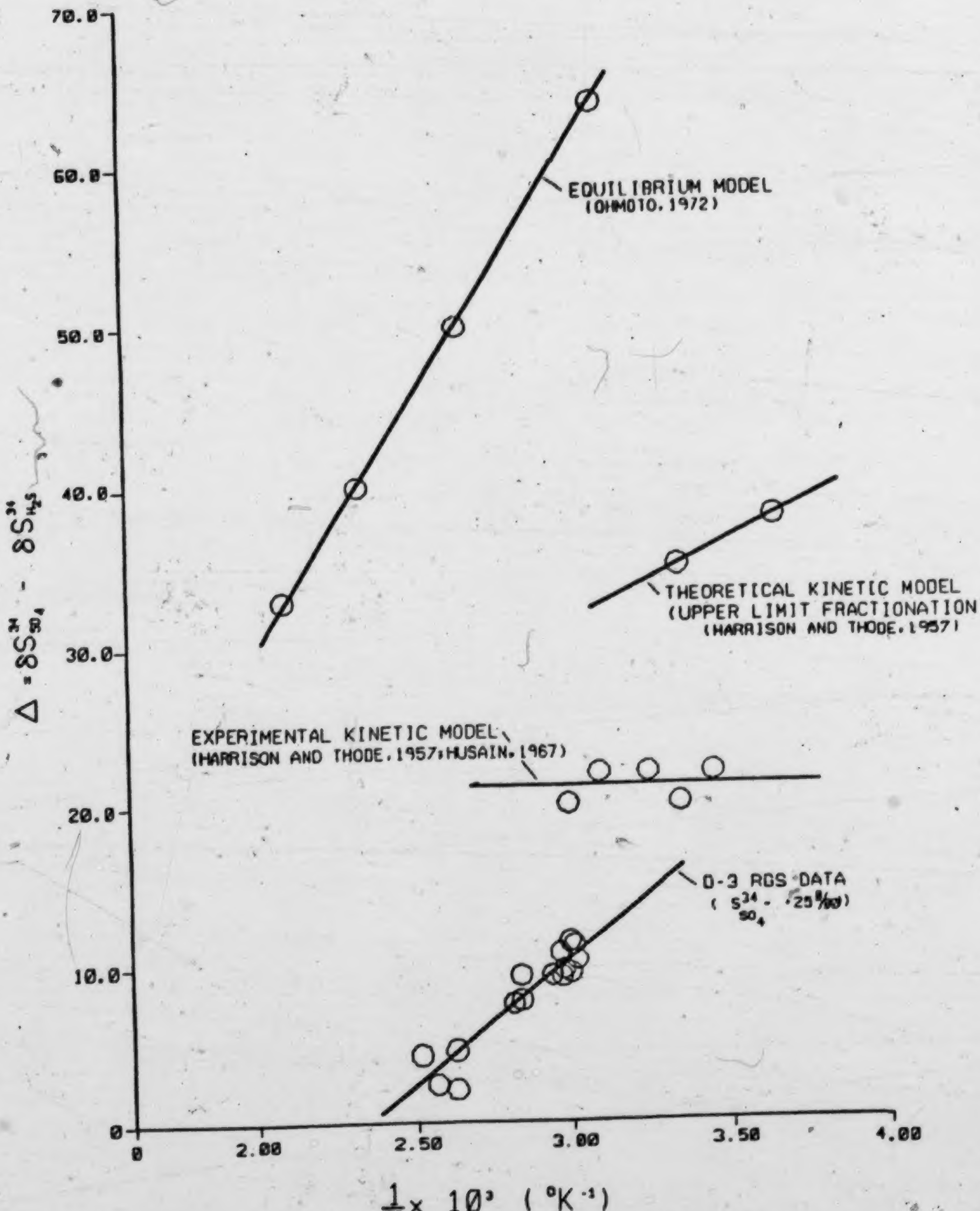
Other open system chemical models have linear relationships between the natural logarithm of the isotope fractionation factor (α), which is approximated by Δ*, and reservoir temperature. For example, the plot of Δ (sulphate-hydrogen sulphide) versus the inverse of absolute temperature for an equilibrium reaction between sulphate and hydrogen sulphide is linear (Sakai, 1968). Also, the theoretical variation of the natural logarithm of the kinetic isotope fractionation factor for the reduction of sulphate to hydrogen sulphide may be a linear function of the inverse of absolute temperature (Harrison and Thode, 1957). However, experimental data reported by Harrison and Thode (1957) and Husain (1967) show that the kinetic isotope fractionation factor involved in the reduction of sulphate to hydrogen sulphide is constant over a temperature range from 18°C to 60°C. Because of the small temperature range (56°C to 124°C) over which Δ varies, for the D-3 RGS data, the plot of Δ vs. T (°C) for the equilibrium and theoretical kinetic models has an apparent linear relationship. In Figure II - 31 examples of the open system equilibrium model, the theoretical kinetic model, and the experimental kinetic isotope model have been plotted in Δ vs. T^{-1} space. For comparison, the D-3 RGS data are included.

---

*$\Delta = (\alpha - 1)\,1000$
Also $\Delta = 1000 \ln\alpha$

FIGURE II - 31

PLOT OF Δ vs 1/T FOR EQUILIBRIUM AND KINETIC ISOTOPE MODELS

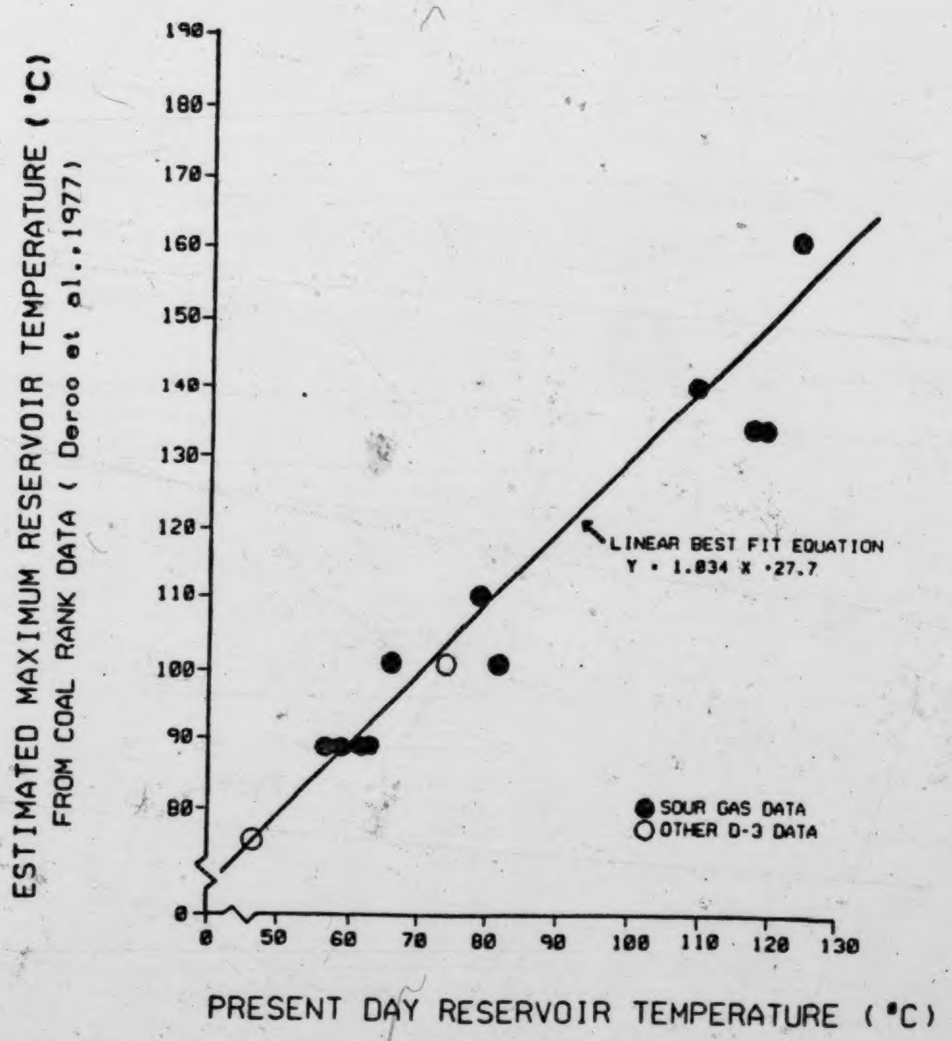


In order for the RGS data to coincide approximately with the equilibrium plot, reservoir temperatures would have to be increased to a range of some 300 to 600°C. A coal rank study by Haquebard (in Deroo et al. 1977) indicates that maximum D-3 reservoir temperatures probably did not exceed present day values by more than 30°C (see Figure II - 32). The range of maximum reservoir temperatures for the D-3 pools studied in this thesis is approximately 80 to 160°C. It is therefore not likely that the equilibrium model applies to the D-3 sour gas system. The similar slope of the theoretical kinetic plot to the D-3 RGS data suggests that the variation of a kinetic isotope fractionation factor with reservoir temperature may be responsible for the RGS isotope trend. Simply not enough is known about the kinetics of sulphate reduction in the hydrocarbon system to identify the reaction responsible for the observed linear trend of the sulphur isotope composition of RGS versus reservoir temperature.

Although the closed system kinetic reduction of sulphate cannot be shown to be the reaction responsible for the generation of sour gases in the D-3 reservoir, a further evaluation of the model gives some insight into sour gas production in the hydrocarbon system. Sulphate lining vugs and pores in the D-3 reservoir rock was chosen as the sulphur source in the closed system model. Alternate sources such as biogenic H_2S, source derived hydrogen sulphide, hydrogen sulphide from the thermal alteration of crude oils and brine sulphate were considered, but are not believed to be major contributors of hydrogen

FIGURE II - 32

PLOT OF PRESENT DAY RESERVOIR TEMPERATURE vs ESTIMATED MAXIMUM RESERVOIR TEMPERATURE, FROM COAL RANK DATA, FOR D-3 POOLS



sulphide to the D-3 system as a whole, for the following reasons.

If brine sulphate were utilized to produce hydrogen sulphide, the chemical system could not be closed. Hitchon (1969a) and Hitchon (1969b) demonstrated that the D-3 oil field brines formed three separate hydrodynamic systems with basin wide communication within each system. As a result the sulphate supply to the hydrocarbon pools would be essentially unlimited. Brine sulphate is therefore a very real sulphur source with a ubiquitous distribution (see Table II - XIV). However, the distribution of sour gas within the D-3 reservoir is restricted. D-3 oil pools along the Stettler-West Drumheller and Wimborne-Duhamel reef trends contain, almost without exception, appreciable contents of hydrogen sulphide in their solution gases and gas caps. For the pools sampled along these trends, the hydrogen sulphide content varied from 1% to in excess of 13%. In contrast the hydrogen sulphide content of the D-3 oil pools along the Homeglen-Rimbey-Redwater system does not exceed 5% and is commonly 0% to trace. For example, Oil Fields of Alberta (1960) reports 0% hydrogen sulphide for the D-3 pools at Acheson, Yekau Lake, Golden Spike, Woodbend, Wizard Lake and Glen Park.

A kinetic study of the reduction of sulphate using hydrocarbon, by Dhannoun and Fyfe (1972), indicates that over a temperature range of 50°C to 200°C the reaction is quite slow. The half life for the reaction at 100°C is 2.62 x 10^{22} years (see Appendix IX).

TABLE II - XIV

Sulphate Concentration* of D-3 Formation Waters

Pool	Sulphate Concentration (mg/l)
Big Lake	895
Acheson	467
Yekau Lake	430
Woodbend	1242
Golden Spike	425
Wizard Lake	293
Glen Park	411
Bonnie Glen	412
Sylvan Lake	Not Available
Westerose	295
West Drumheller	974
New Norway	1126
Buffalo Lake	0.2
Bashaw	414
Erskine	513
Stettler	596
Malmo	584
Clive	434
Wimborne	472

Although this reaction is slow it could produce enough hydrogen sulphide to initiate a more rapid Toland (1960) type reaction. The Toland reaction will go in both acid and basic media (refer to Toland, 1960) but achieves its greatest potential at low pH's. Therefore, any system which has sulphate in contact with hydrocarbon has the ability to generate hydrogen sulphide. The limited area of the hydrocarbon - water interface together with the observation that interchanges across it are often restricted by pore throat plugging due to calcite cementation (Racz, 1972) and gas deasphalting makes this interface unfavorable for the production of significant volumes of hydrogen sulphide in comparison to the hydrocarbon pore system.

---

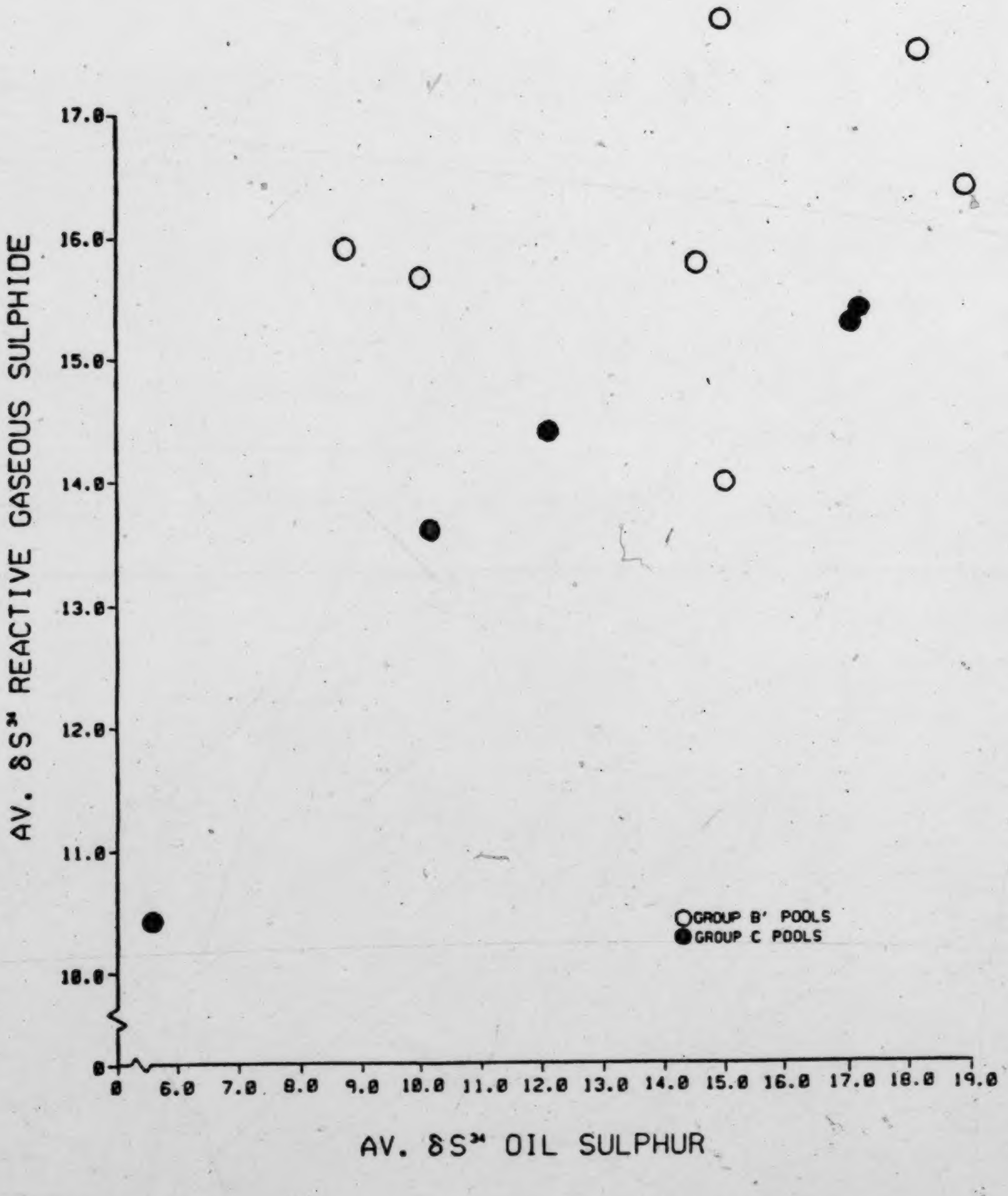
*Data has been taken from Oil Fields of Alberta (1960), Oil Fields of Alberta Supplement (1966) and Hitchon et al. (1971).

The relative area of the pore system in contact with hydrocarbon is many times greater than the area of the hydrocarbon - water interface. Communication between the hydrocarbon and the D-3 reservoir rock (limestone or dolomite) in the pore system is through a layer of pendant water of variable thickness which wets the pore surfaces. Secondary anhydrite or gypsum coating the pore surfaces could restrict the operation of the carbonate buffer. The reaction between sulphate ions in the pendant water and dissolved hydrocarbon could then provide enough hydrogen sulphide to initiate the Toland reaction which would further lower the pH of the pore water to some low equilibrium or steady state value which favors a more rapid sulphate reduction. Hydrogen sulphide production would stop or become vastly decreased when most of the sulphate coating the pore surfaces was reduced, allowing contact of the carbonate reservoir with the acid pore water, raising the pH. A closed system sulphur isotope effect would be observed in the hydrogen sulphide product if the rate of sulphate ion exchange between the pendant water and the anhydrite in the pore coating was much greater than the rate of sulphate reduction. This would in effect produce a sulphate pore coating whose outer surface had the same sulphur isotope composition as the aqueous sulphate ion.

In Figure II - 33 the sulphur isotope composition of oil sulphur has been plotted against the sulphur isotope composition of RGS for the D-3 oil pools. Only the Group C pools show a correlation between these variables. This correlation is consistent with the conclusion that the Group C oils have undergone sulphurization. As a result, the gaseous sulphur system in the West Drumheller, Erskine, Stettler and Buffalo Lake pools may have lost sulphur to their oils and are therefore not closed systems. The effect of the sulphur loss on the sulphur isotope composition of RGS would depend on the fraction lost. The Group B' pools show a random scatter of data points in Figure II - 33 and the D-3 gas pools at Strachan, Ricinus, Harmattan, Pine Creek and Pine N.W. were probably never associated with an oil phase. Therefore the D-3 pools studied probably never received a significant contribution of sulphur from the thermal alteration of a sulphurous oil phase. The sulphur content within the D-3 oils studied is regarded as a product of sulphurization by hydrogen sulphide, polysulphides and native sulphur and not as a source for those compounds (see Ho _et al_. 1974). It is unlikely that over the range of maximum reservoir temperatures attained by the D-3 oils (85 - 110°C; see Deroo _et al_. 1977) that desulphurization would occur. In general, crude oil should be more reactive to "sulphur" (H_2S, H_2S_x, S_8) as reservoir temperature increases. Furthermore, many reactions between organic compounds and "sulphur" proceed

FIGURE II - 33

PLOT OF δS^{34} GAS SULPHUR vs δS^{34} OIL SULPHUR FOR D-3 REEFS



over a temperature range of 100 - 300°C forming stable organosulphur compounds such as dibenzothiophenes and thiols (Pryor, 1962). The difference in correlations between the sulphur isotope composition of RGS and oil sulphur in Figure II - 33 can be interpreted as the result of a difference in activation energies between the oil sulphurization and hydrogen sulphide generation reactions together with a limited, composition dependent, capacity of a crude oil to react with sulphur. At lower temperatures it is unlikely that the oil sulphur and gas sulphur systems can interact sufficiently to saturate the reactive sites (some hydrocarbons and heteroatomic compounds; see Bestougeff and Combaz, 1973) within the oil. However, the two systems can interact, provided that reservoir temperature is not too low, and as a result the sulphur isotope composition of the gas and oil sulphur systems should be interdependent. Group C oils can be cited as an example of this low temperature case. At higher reservoir temperatures the reactive sites in the oil would soon become saturated and the oil and gas sulphur systems could further interact only on a very limited basis at these comparatively low temperatures. The gas sulphur system could however continue to evolve through a Toland type reaction. A sulphur isotope dependence between the gas and oil sulphur systems should only be observed at an early stage prior to or just after the oils became saturated with sulphur. The Group B' oils may be an example of a mature stage of this second case and therefore show no sulphur isotope dependence between RGS and oil sulphur. Because of the limited experimental data on the interaction of the oil and gas sulphur systems, the above discussion is speculative, and based mainly on the experiments of Bestougeff and Combaz (1973) and data from Pryor (1962).

In the opinion of Orr (1975) and Kaniwisher and Ostlund (in Jensen, 1962) hydrogen sulphide which has been generated in the source by such processes as early biogenic sulphate reduction, thermal degradation of sulphurous organic matter or inorganic sulphate reduction, has little potential to migrate to the reservoir. This conclusion is based on the reactivity of H_2S, HS^- and S^{-2} to iron in the source shales (see also Berner, 1969). Not until all ferrous and ferric iron in the shales and along the primary migration paths has been reacted to form any of the intermediate unstable iron sulphides such as mackinawite, greigite or pyrrhotite (Berner, 1962, 1964 and 1967) would reactive sulphide migrate to the reservoir. Furthermore, the comparatively rapid conversion of these intermediate iron sulphides to refractory pyrite (Berner, 1970) stabilizes shale sulphide preventing much desulphurization as source temperature increases. The identification of an adsorbed hydrogen sulphide phase in source rocks by Le Tran _et al_. (1973) suggests that it is possible to saturate all iron with sulphide and retain hydrogen sulphide as a weakly bonded compound to clay mineral surfaces. As formation temperature increases, this adsorbed sulphide phase may be released from the source rocks. The volume of adsorbed hydrogen sulphide that could migrate to the reservoir is uncertain. Oils that are sulphurized in the source and then migrate to the reservoir could give up their sulphur as gaseous sulphide during organic metamorphism. However, it is unlikely that any of the D-3 oil pools studied have experienced temperatures high enough to have undergone desulphurization.

The lack of significant depletion of the D-3 oil n-paraffins together with unfavorably high present day reservoir temperatures suggests that the biological reduction of brine sulphate is not a process that could produce significant volumes of hydrogen sulphide and related sulphide compounds in the D-3 reservoir system studied (see Part II, Chapter II, Section I).

The sulphur isotope fractionation factor for the kinetic reduction of sulphate in the closed system model was chosen as 1.022 on the basis of experimental work reported in papers by Harrison and Thode (1957) and Husain (1967). Both these papers demonstrated that the isotope fractionation effect is apparently independent of temperature. Harrison and Thode (1957) identified this fractionation effect with the rate controlling step of the first S-O bond rupture of sulphate to produce sulphite. Data reported by Husain and Krouse (1976) are particularly relevent to the Toland (1960) reaction. Husain and Krouse (1976) studied the sulphur isotope fractionation effects involved in the reduction of sulphate by hydrogen sulphide in sulphuric acid solutions at pH values less than 1. These solutions were much more acid than the media used by Toland, and no organic matter was included.

The results reported by Husain and Krouse (1976) can be explained in terms of the reactions discussed by Toland (1960) although the end products (SO_2 and S°) are not those observed by Toland (H_2S, S°, carboxylic acids and CO_2). The difference in the products is probably the results of the exclusion of organic matter from the chemical systems studied by Husain and Krouse (1976). According to Toland (1960) sulphate reduction proceeds through the following two reactions:

$$SO_4 + H_2S \xrightarrow[\text{Medium}]{\text{Acid}} S_2O_3^{=} + H_2O \qquad \text{II - 19}$$

$$S_2O_3^{=} \xrightarrow[\text{Medium}]{\text{Acid}} S^\circ + SO_3^{=} \qquad \text{II - 20}$$

Data from Husain and Krouse (1976) show that the sulphur isotope fractionation effects that may be associated with these two equations are consistent with one way kinetic oxidation - reduction reactions and not equilibrium exchange reactions as proposed by Toland (1960). Since no organic matter was included in the experiments by Husain and Krouse (1976), Toland's sulphite reduction reaction ($SO_3^{=}$ + organic matter $\longrightarrow$ $H_2S + CO_2$ + carboxylic acids - see also Part II, Chapter I of this thesis) could not occur. A possible substitute reaction is:

$$SO_3^{=} + 2H^+ \xrightarrow[\text{Medium}]{\text{Acid}} SO_2 + H_2O \qquad \text{II - 21}$$

This is consistent with the fact that SO_2, like CO_2, is a weak acid gas. Husain and Krouse (1976) reported that elemental sulphur was enriched in sulphur 32 by 3.7^o/oo with respect to hydrogen sulphide, and sulphur dioxide was enriched in sulphur 32 by 17.9°/oo with respect to the initial sulphate composition. The isotope enrichment for the kinetic reduction of sulphate reported by Harrison and Thode is 22°/oo (the product H_2S being enriched in S^{32}). Therefore, SO_2 derived from the reduction of sulphate by hydrogen sulphide is some 4.1°/oo more enriched in S^{34} than would be expected from Harrison and Thode's data. When the compounded error of analysis (± 0.4°/oo) is considered, this difference is indistinguishable in magnitude and sign from the S^{32} enrichment in the native sulphur associated with the sulphur dioxide. Therefore the sulphur isotope results from Husain and Krouse (1976) can be interpreted to indicate that sulphur dioxide sulphur has been derived mainly from sulphate through a reduction reaction with an associated fractionation factor of 1.022. Hydrogen sulphide sulphur has been incorporated mainly into the elemental sulphur product. Sulphur dioxide and elemental sulphur contain minor amounts of hydrogen sulphide and sulphate sulphur, respectively, through the thiosulphate decomposition reaction. That is, there is a sulphur fractionation factor of about 1.004 for equation II - 20. Husain (1967) and Husain and Krouse (1976) proposed similar conclusions.

It is apparent that the use of one isotope fractionation factor in the simple closed system model does not adequately describe the isotope behavior of the sulphur system. A further kinetic fractionation may occur when the thiosulphate ion decomposes to native sulphur and sulphite. Furthermore, isotope exchange reactions between H_2S, $SO_3^=$

and $S_2O_3^=$ are possible (Husain, 1967). The closed system isotope model developed in this thesis is a simple treatment of a potentially complex hydrocarbon-sulphur system. At its very best, this model may only describe an average behavior.

c) The Hydrocarbon Sulphur System - A Model for the generation of H_2S

The design of a general model for the generation of hydrogen sulphide in the reservoir system and the sulphurization of crude oils is complicated by a multiplicity of sulphur sources and the complex nature of the organosulphur system reactions. Considerable emphasis in this thesis has been placed on reservoir sulphate, through the Toland reaction, as the major source for sulphur compounds. Other sources for sulphur in oil and gas pools have been proposed. Le Tran (1971) and Le Tran et al. (1973).concluded from a study of Cretaceous source rocks in the Aquitaine Basin, that the sulphur content of the oils and natural gases was derived from the desulphurization of original marine organic matter. As an example, Le Tran (1971) cited data published by Bowen (1966) which indicated that some marine algae contain up to 9% sulphur. Le Tran et al. (1973) concluded that the majority of the hydrogen sulphide was produced from the Cretaceous source shales during the main phase of gas generation which occurred at present day reservoir temperatures between 110°C to 120°C. These authors also demonstrated that the source rocks contained hydrogen sulphide that was not fixed by transition metal cations but was weakly bonded to clay mineral surfaces. This gas acted as a source of sulphur during primary migration. Granch and Posthuma (1973) concluded from a study of Venezuelan oils and source rocks that oils generated from sulphurous source rocks should contain sulphur in varying amounts dependent on the intensity of maturation of the source sediments. Hitchon (1968) proposed that the hydrogen sulphide content of the Leduc D-3 reefs was derived from the maturation of the source rocks (Ireton and Duvernay shales). The sulphur content in these shales was presumed to have been generated from bacterial sulphate reduction at an early stage of deposition. Ho et al. (1974) and Evans and Staplin (1971) concluded that the thermal maturation of oil pools, whose sulphur contents are unstable at higher reservoir temperatures, could generate substantial concentrations of hydrogen sulphide. The biodegradation of crude oil by sulphate reducing bacteria has been proposed as a sulphur source for shallow reservoirs (Bailey et al. 1973). Studies by Postgate (1960, 1965), Trudinger et al. (1972) and by Orr (1973) indicate that sulphate reducing bacteria metabolize low molecular weight alcohols and acids as well as molecular hydrogen. These compounds are all products which are generated from the fermentation of carbohydrates by other anaerobic microorganisms. Harwood (1973) and Jobson (1976) concluded that sulphate reducing bacteria cannot metabolize crude oil directly, but utilize the metabolic products generated by aerobes and other anaerobes which can degrade the oil. Therefore, biogenic sulphide generated from the metabolism of crude oil is restricted to shallow low temperature

(<60°C) reservoirs whose hydrocarbons are being actively degraded by a population of aerobic and anaerobic non-sulphate reducing bacteria.

All of the above proposed sources for sulphur and sulphurization reactions (with the exception of bacterial sulphate reduction) have the potential to provide enough sulphur to account for the contents of hydrogen sulphide and organosulphur compounds in the D-3 pools. The arguments used in this thesis to support the Toland reaction in favor of the others are not conclusive. Even the correlation between the isotope composition of RGS and D-3 reservoir temperature does not conclusively demonstrate the occurrence of a temperature dependent isotope effect associated with the generation of hydrogen sulphide in the oil pool. This correlation could result from a diffusion isotope fractionation incurred during the updip migration of hydrogen sulphide generated in the metamorphosed zone from sulphurous crude oils and/or sulphur rich organic source matter. Several facts must be established before the D-3 sulphur source and the sulphurization process can be identified.

First, if the source rocks are the sulphur source, a potential for these to generate sulphur must be established as well as a link between the source and reservoir sulphur systems. This can be done by measuring the content of the fixed sulphide (acid soluble sulphur), elemental sulphur, sulphate, organosulphur and adsorbed hydrogen sulphide (see Le Tran, 1971) in the source rocks and correlating these values with the sulphur content in the adjacent gas and oil pools. A sulphur isotope comparison of the various source and oil-gas pool sulphur compounds would provide valuable supporting evidence.

Second, if the maturation of the oil phase is to provide a pool with hydrogen sulphide and more mature (thermally stable) organosulphur compounds, it must be demonstrated that the oil has undergone thermal alteration greater than that experienced during its sulphurization. In the case of the D-3 pools studied, their period of most intensive thermal alteration was probably reached during their primary generation from the Ireton and Duvernay shales in the Upper Cretaceous (Deroo _et al_. 1977). Subsurface temperatures since then have been lower mainly due to denudation. It is therefore difficult to argue that the _in situ_ maturation of a sulphurous oil is responsible for the generation of H_2S, HS^-, H_2S_n, and S_8 in the D-3 system. Sulphur isotope and oil composition data, reported in this thesis, support sulphurization of the oils rather than desulphurization.

Finally, if the Toland reaction does occur in the reservoir system, so called, native state cores from the producing zone of sour pools should have irreducible pore waters that contain substantial amounts of sulphate, sulphite or thiosulphate and carboxylic acids. The sour oils should have much higher contents of organic acids than sweet oils from the same family and level of maturity. Furthermore, carbon dioxide in the gas cap and solution gas phase should have its δC^{13} and δO^{18} values measured and compared to the δC^{13} and δO^{18} values of, respectively, hydrocarbon, and sulphate lining pores and vugs and in formation waters. A close similarity in these isotope values would be a strong argument in favor of the Toland reaction.

Hydrogen sulphide, bisulphide, sulphide, elemental sulphur, sulphanes (hydrogen polysulphides), sulphite and thiosulphate can be considered as the major inorganic products from desulphurization reactions. Ho et al. (1974) discuss the behavior of organosulphur compound groups during the thermal alteration of sulphurous crude oils. The various organosulphur products result from either transformations from less stable to more stable sulphur compounds or from sulphurization reactions resulting from the interaction of crude oil with the inorganic sulphur products. The abundance of the inorganic sulphur compounds in the reservoir and source rocks is dependent on the type of sulphur source, the nature of the desulphurization reactions, and on the Eh and pH of the system.

A paper by Boulegue (1973) outlined the following sulphur system reaction scheme (see Figure II - 34a). This diagram can be modified to include hydrogen sulphide, the effect of the partial oxidation of bisulphide or H_2S by ferric iron and the general effects of the variations of Eh and pH (see Figure II - 34b). The interaction of hydrogen sulphide, polysulphide, bisulphide and elemental sulphur

FIGURE II - 34 - A

SULPHUR SYSTEM REACTION SCHEME I
(AFTER BOULEGUE, 1973)

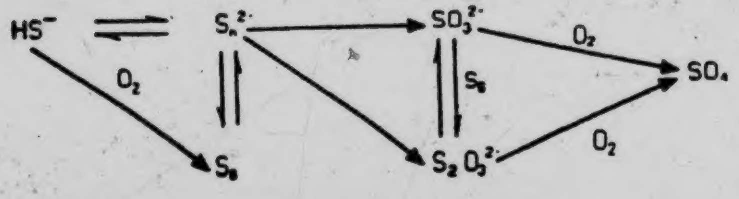
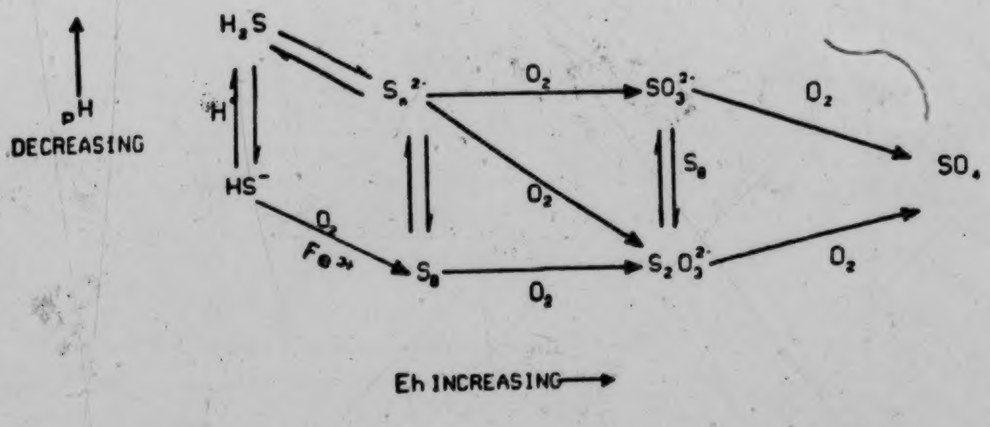

HS⁻
S_n²⁻
SO₃²⁻
O₂
SO₄
O₂
S₈
S₈
S₂O₃²⁻
O₂

FIGURE II - 34 - B

SULPHUR SYSTEM REACTION SCHEME II
(MODIFIED SCHEME I)


H₂S
S_n²⁻
O₂
SO₃²⁻
O₂
pH
DECREASING
H⁺
HS⁻
S₈
O₂
SO₄
O₂
Fe³⁺
S₈
O₂
S₂O₃²⁻
O₂
Eh INCREASING

results in the stablization of Eh and pH through either steady state or equilibrium reactions (Berner, 1963 and Boulegue, 1973). Hyne (1968), Muller and Hyne (1969) and Swift (1976) have demonstrated that elemental sulphur, hydrogen sulphide and sulphanes (mainly $H_2 S_9$) coexist in sour gas reservoirs. It is therefore likely that the oxidation-reduction potential and the hydrogen ion content of sour gas reservoirs is stabilized at some equilibrium or steady state reducing and acidic value.

The reaction scheme in Figure II - 34b can be expanded and rewritten to form a general model which demonstrates the potential of a Toland type reaction to generate hydrogen sulphide and related sulphur compounds in a hydrocarbon bearing reservoir (see Figure II - 35). In this model, an initial amount of hydrogen sulphide reacts with reservoir sulphate to generate thiosulphate which disproportionates to sulphite and native sulphur. The oxidation of hydrocarbon by sulphite-thiosulphite produces hydrogen sulphide, carboxylic acids, carbon dioxide, organosulphur compounds, asphaltenes, aromatics and elemental sulphur. Elemental sulphur (S_8) is an important product capable of reacting with the oils, sulphurizing them further, and capable of reacting with hydrogen sulphide forming sulphanes which interact to stabilize the Eh and pH of the reservoir system. Since hydrogen sulphide is both a reactant and a product, the reaction is self perpetuating until the sulphate pore coating is depleted enough to give the acid pore waters access to the limestone reservoir rock. As a result, the effect of the sulphur system buffer diminishes and the pH of the system increases (see Garrels and Christ, 1965) stabilizing the remaining sulphate. In Figure II - 35 the carbonate-hydrogen ion interaction is dashed to indicate the uncertainty of the effectiveness of the carbonate buffer due to a partial or complete dolomitization of the reservoir rock or due to the isolation of a limestone reservoir rock from formation fluids by silica, anhydrite or insoluble residues lining vugs and pore surfaces.

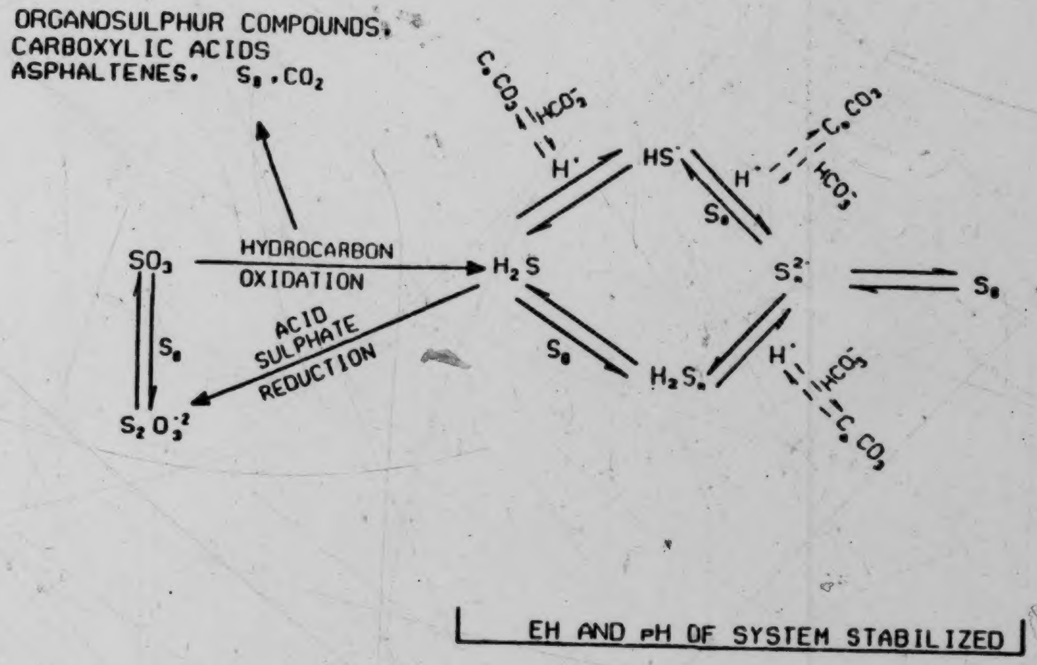
Most of the factors (listed at the top of Figure II - 35) that are required to initiate the Toland reaction can be achieved easily in the D-3 reservoir system. Deep formation waters have generally low oxygen contents (negative Ehs) and the sulphate concentration in the D-3 oil field brines (see Table II - XIV) should be high enough to support a Toland-type reaction. The pH of the D-3 reservoir waters has been reported by Hitchon et al. (1971) to vary between 5.98 and 7.31 for 18 D-3 pools sampled. However, the authors noted that these values may not be indicative of the true pH of the formation waters. The initial concentration of hydrogen sulphide could be generated from the reduction of sulphate by organic matter (Dhannoun and Fyfe, 1972) or from the migration of hydrogen sulphide, bisulphide and sulphanes generated during the thermal maturation of the source rocks. This latter sulphur source is of uncertain value due to the high reactivity of the sulphides to transition metal cations (Orr, 1975). Since the conditions required for the initiation of the Toland sulphate reduction

FIGURE II-35

REACTION SCHEME III-
THE TOLAND MODEL FOR THE GENERATION OF
SULPHUR COMPOUNDS IN THE HYDROCARBON RESERVOIR SYSTEM

REQUIREMENTS:

ACIDIC-REDUCING AQUEOUS MEDIUM (Eh < - 0.1; pH; < 7)
HYDROCARBON (OIL OR GAS)
SULPHATE (OIL FIELD BRINE SULPHATE OR ANHYDRITE COATING PORES AND VUGS)
HIGHER RESERVOIR TEMPERATURES
AN INITIAL AMOUNT OF HYDROGEN SULPHIDE


ORGANOSULPHUR COMPOUNDS,
CARBOXYLIC ACIDS
ASPHALTENES. S_8, CO_2
SO_3
HYDROCARBON
OXIDATION
S_8
ACID
SULPHATE
REDUCTION
$S_2O_3^{-2}$
H_2S
C, CO_3
HCO_3^-
H^+
HS^-
H^+
C, CO_3
HCO_3^-
S_8
S_8
S_x^{2-}
S_8
H_2S_x
H^+
HCO_3^-
C, CO_3
EH AND pH OF SYSTEM STABILIZED

reaction are apparently easily attainable in the D-3 reservoir system, the observation that many of the oil pools along the Homeglen-Rimbey-Redwater reef trend contain very low to zero contents of hydrogen sulphide and organosulphur compounds is difficult to explain. One solution to this problem has been presented in this thesis. That is, the sulphate reduction reaction is restricted to reservoirs that have sulphate lining pores and vugs. This anhydrite layer would provide a source of sulphur in intimate contact with the hydrocarbon phase and restrict the operation of the carbonate buffer.

The occurrence of sulphur wells in the Panther Dome area of the Albertan foothills provides an example of the near complete oxidation of a natural gas pool by Toland type reactions (see Hunt, 1975). Dry gas pools in the metamorphosed facies have hydrocarbon assemblages which generally consist of 98% methane and 1 to 2% ethane. Hydrogen sulphide contents may vary from nil to as high as 86% (by volume) of the total gas (Larson, 1969). Carbon dioxide is often a comparatively abundant associated gas (Evans and Staplin, 1971; and Hitchon, 1963). Examples of gas analyses from metamorphosed reservoirs are shown in Table II - XV. The following Toland reactions may occur in the sour metamorphosed dry gas reservoirs:

$$\begin{array}{ll} 2H^+ + H_2S + SO_4^{-2} \longrightarrow & H_2S_2O_3 + H_2O \\ & \quad \downarrow\!\uparrow \\ & S + H_2SO_3 \end{array}$$

$$CH_4 + H_2S_2O_3 \longrightarrow 2H_2S + CO_2 + H_2O$$

$$C_2H_6 + 2H_2S_2O_3 \longrightarrow 3H_2S + 2CO_2 + 2H_2O + S$$

$$S_8 + H_2S \rightleftharpoons H_2S_9$$

These reactions show that the entire hydrocarbon content of a gas pool can be oxidised producing sulphur deposits consisting of elemental sulphur, hydrogen sulphide, sulphanes and carbon dioxide.

TABLE II - XV

Natural Gas Analyses (Volume %) from Metamorphosed Reservoirs

Pool Well Description Producing Zone	Panther River 5-19-30-10W5 Devonian	Pine Creek 2-10-58-19W5 Leduc (Devonian)	Beaver River Pan Am A-2 d-73-K Nahanni (Devonian)
Hydrogen	-	-	
Methane	24.55	67.74	89.65
Ethane	0.18	0.57	0.15
Propane	0.06	0.15	
Isobutane	Trace	0.04	
n-Butane	Trace	0.06	
i-Pentane	Trace	0.03	0.01
n-Pentane	Trace	0.03	
Hexanes	Trace		
Heptanes$^+$	0.16	0.35	
Octanes$^+$			
Nitrogen	0.84	0.61	4.77
Helium		-	-
Carbon Dioxide	3.79	4.88	5.04
Hydrogen Sulphide	70.42	25.54	0.38
Totals	100.00	100.00	100.00

In conclusion, the Toland reaction cannot be conclusively demonstrated as responsible for the production of major amounts of hydrogen sulphide and sulphur compounds in the D-3 reservoir system. However, this reaction forms a redox couple which over geologic time has the potential to generate an abundance of sulphur compounds over a fairly wide range of reservoir temperatures. The reaction is self sustaining and can establish its own favorable chemical environment through sulphide equilibria.

Section 3: Carbon Isotope Composition of D-3 Natural Gases

The carbon isotope composition of the methane, ethane and propane contents of D-3 natural gases is summarized in Figure II - 36 and Table II - XVI (see also Appendix VIII). Analyses from the Lower Devonian Keg River Formation at the Rainbow and Zama oil fields and from the equivalent Nahanni Formation at Beaver River have been included for comparison.

On the average, D-3 methane, ethane and propane are more enriched in C^{12} than the average associated oil by 16.5, 8.1 and 4.2 per mil respectively. For every natural gas analysed the trend (noted by Silverman, 1967) δC^{13} (methane) $<\delta C^{13}$ (ethane) $<\delta C^{13}$ (propane) was observed. Reversals of this trend [that is, δC^{13} (propane) $<\delta C^{13}$ (ethane) or δC^{13} (ethane) $<\delta C^{13}$ (methane)] predicted from theoretical calculations by Smith et al. (1971) and noted by Erdman and Morris (1974), were not observed in this study.

The carbon isotope composition of methane is generally considered to reflect the marine or terrestrial origin (Stahl, 1977) of the source rock organic matter and the maturation index of the gas source (Harwood, 1973). In Figure II - 37 the carbon isotope composition of methane has been plotted against the maturation-sensitive ratio

FIGURE II-36

CARBON ISOTOPE VALUES FOR D-3 AND KEG RIVER NATURAL GAS COMPONENTS

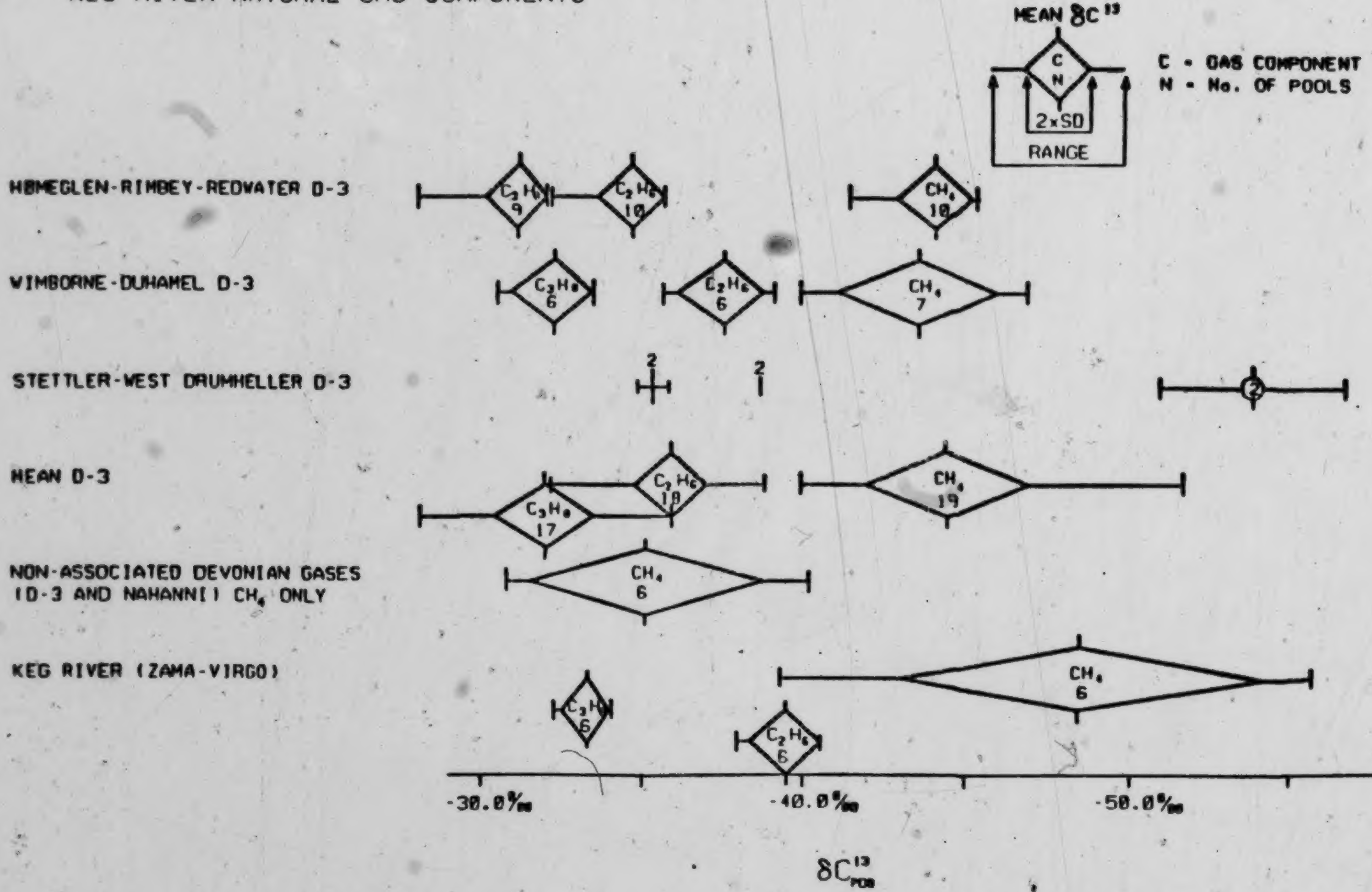


TABLE II - XVI

Average δC^{13} Values for Devonian Oil and Gas Pools

Pool Name		Reservoir Temp °C	$\frac{C_1}{C_1 + C_2}$	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Big Lake	D-3	58	0.751	-27.3	-29.0	-26.2	-45.4	-35.7	-31.9
Acheson	D-3	60	0.781	-28.5	-29.4	-28.2	-43.8	-35.2	-32.1
Yekau Lake	D-3	63	0.781	-28.5	-29.5	-28.3	-43.6	-34.8	-32.0
Leduc Woodbend	D-3	66	0.794	-28.4	-29.4	-28.2	-43.6	-34.4	-30.5
Golden Spike	D-3	67	0.764	-27.3	-28.7	-26.4	-45.9	-35.7	-32.1
Wizard Lake	D-3	72	0.786+	-28.3	-29.3	-27.5	-45.1	-35.9	-29.9(?)
Glen Park	D-3	74	0.814+	-28.0	-28.9	-27.1	-45.0	-35.6	-31.3
Bonnie Glen	D-3	77	0.832+	-	-29.5	-28.1	-44.7	-33.9	-
Sylvan Lake	D-3	79	0.937	-	-	-	-41.3	-32.2	-29.3

+Value based on one gas analysis.

The standard deviation associated with the $C_1/C_1 + C_2$ ratio is on the average 0.033.

Table II - XVI (Cont'd)

Pool Name		Reservoir Temp °C	$\frac{C_1}{C_1 + C_2}$	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Westerose	D-3	82	0.824	-28.4	-29.4	-28.1	-44.9	-33.9	-30.7
Redwater	D-3	34	0.801	-	-	-	-53.5	-	-
West Drumheller	D-3	57	0.773	-	-30.1	-27.8	-51.8	-38.7	-35.9
New Norway	D-3	58	0.780	-	-28.4	-27.3	-45.9	-38.7	-33.8
Buffalo Lake	D-3	57	0.863	-	-29.7	-25.2	-43.7	-36.8	-33.0
Bashaw	D-3	61	0.881	-	-29.6	-26.7	-43.0	-36.1	-31.0
Erskine	D-3	62	0.915	-27.1	-28.8	-26.6	-42.6	-35.8	-32.2
Stettler	D-3	63	0.809	-27.5	-28.9	-26.8	-46.2	-38.8	-35.0
Malmo	D-3	63	0.834	-	-30.0	-	-45.0	-37.8	-33.8
Clive	D-3A	66	0.848	-	-29.5	-27.8	-42.0	-37.8	-30.7
Wimborne	D-3	79	0.952	-	-29.1	-28.1	-40.0	-	-
Zama Keg River		-	-	-28.0	-29.0	-27.6	-50.3	-39.7	-33.1
Virgo Keg River		-	-	-28.4	-29.6	-28.0	-45.6	-38.9	-33.6

The standard deviation associated with the $C_1/C_1 + C_2$ ratio is on the average 0.033.

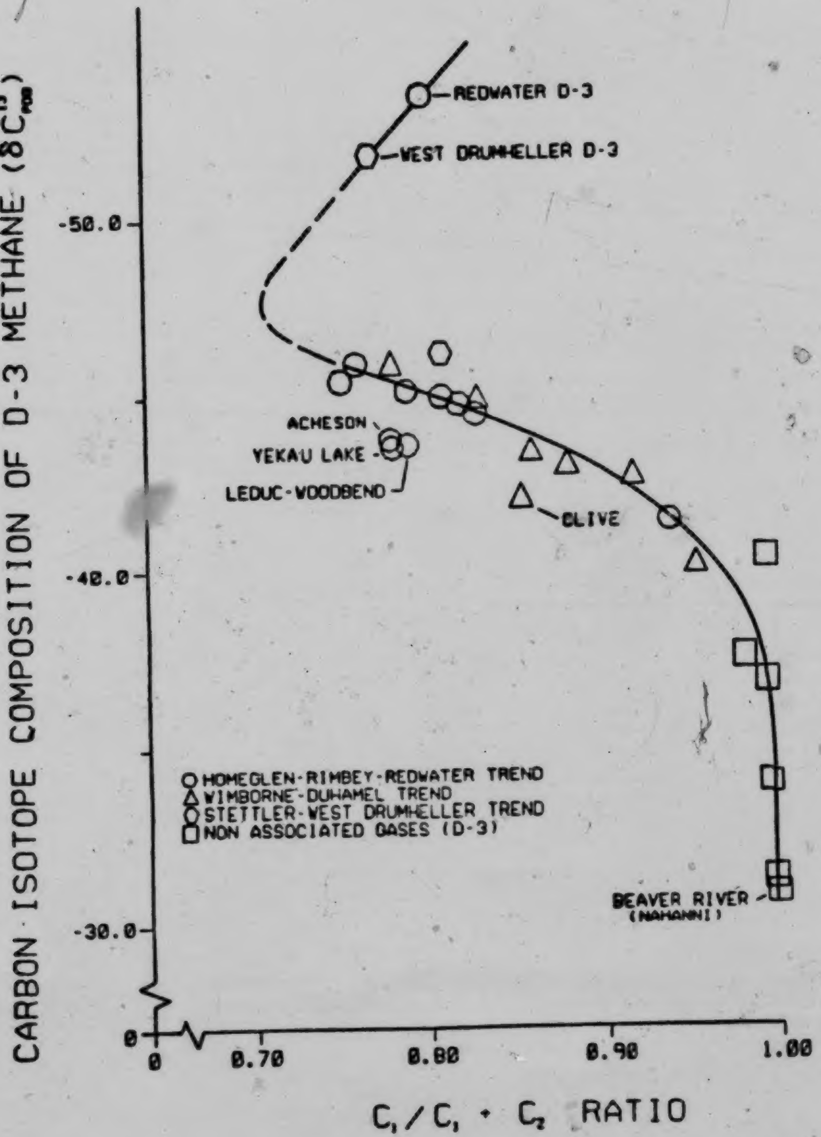
Table II - XVI (Cont'd)

Pool Name		Reservoir Temp °C	$\frac{C_1}{C_1 + C_2}$	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Rainbow Keg River		-	-	-28.7	-29.7	-28.0	-	-	-
Ricinus	D-3	107	0.994	-	-	-	-40.3	-	-
Strachan	D-3	124	0.980	-	-	-	-37.5	-27.2	-24.1
Harmatten E	D-3	110	0.994	-	-	-	-31.2	-	-
Pine Creek	D-3	117	0.992	-	-	-	-36.8	-	-
Pine N.W.	D-3	119	0.994	-	-	-	-33.9	-	-
Beaver River Nahanni		171	0.998	-	-	-	-30.9	-	-

The standard deviation associated with the $C_1/C_1 + C_2$ ratio is on the average 0.033.

FIGURE II - 37

PLOT OF THE CARBON ISOTOPE VALUE (δC^{13}_{PDB}) OF D-3 METHANE vs $C_1/C_1 + C_2$ RATIO



$C_1/C_1 + C_2$* (see Feux, 1977) for the D-3 natural gases. With the exception of the Redwater and West Drumheller methanes the remaining D-3 methanes, including the Beaver River Nahanni samples, plot along a continuous curve of increasing maturity, or an increasing $C_1/C_1 + C_2$ ratio. Natural gases like those from Strachan, Ricinus, Harmattan and Beaver River, whose carbon isotope del values lie between -40 to -25°/oo and whose hydrocarbon composition consists of methane in excess of 95%, are classed as deep dry gas. These gases are believed to have been produced from overmature source rocks and metamorphosed oil pools. The remaining D-3 gases have methane carbon isotope values that range from -58°/oo to -40°/oo and contain significant volumes of C_2^+ hydrocarbons. Such gases are classed as gases associated with oil generation and are considered to have been produced from mature source rocks or from the maturation of crude oil. A third group of natural gases, termed shallow dry gases, contains in excess of 98% methane. The carbon isotope values of the methane range from -75°/oo to -58°/oo. This gas is believed to be produced by methane generating bacteria (Feux, 1977). A subgroup, termed mixed gases (see Harwood, 1973), possesses characteristics from both the shallow dry gases and gase associated with oil generation. The West Drumheller and Redwater natural gases have been placed in this subgroup due to their deviation from the main D-3 plot in Figure II - 37. However, their propanes-plus content and their methane carbon isotope values place them in the group of gases associated with oil generation. West Drumheller and Redwater natural gases have more methane and lighter (more C^{12} - enriched) methane del values than the other D-3 gases associated with oil generation. These compositions could be achieved by mixing biologically and thermally generated methanes. However, the high salinities of the D-3 formation waters at West Drumheller and Redwater (respectively 113,200 and 101,681 ppm T.D.S.) and their reservoir pressures (refer to Oil and Gas Conservation Board of Alberta, publication #70-22, 1970) class these pools with the deep basin D-3 reef systems. It is possible that the West Drumheller and Redwater natural gases have been produced by a different thermochemical (as opposed to biological) low temperature reaction which generates larger quantities of more C^{12} - enriched methane. Stahl (1974) is of the same opinion, however his study rejected the use of solution gases. Therefore, at a $C_1/C_1 + C_2$ ratio of around 0.70 and carbon del values near $-46.0^{o}/oo$ the basic nature of the thermochemical methane generation reaction may change. The mixed gas subgroup may be produced by this hypothesized low temperature thermochemical reaction, although truly mixed biological and thermal gas deposits probably do exist (Harwood, 1973).

---

*C_1 = Methane; C_2 = Ethane and C_3 = Propane

Another interpretation of the relationship of the Redwater and West Drumheller natural gases to the other D-3 gases can be given in terms of migration. These two pools are the shallowest of the D-3 pools studied. As a result they have the lowest reservoir temperatures and have probably had the longest migration paths from the gas source in the metamorphosed zone, down dip, to the reservoir trap. The long migration path would produce a natural gas whose bulk composition would be comparatively enriched in methane and C^{12}. At the lower reservoir temperatures, comparatively lower volumes of thermal gas would be produced by the in situ maturation of the associated oil phase, which would dilute the migrated gas. Therefore any migration fractionation effects would be most likely observed in the Redwater and West Drumheller pools. As shown in Figure II - 37 the West Drumheller and Redwater natural gases have comparatively more C^{12} - enriched methane.

According to Stahl (1975, 1977) methane derived from the maturation of organic matter from sapropelic marine environments is 10-15 per mil more enriched in C^{12} than methane derived from continental organic matter. The uniform plot of the carbon isotope composition of D-3 methanes in Figure II - 37 and the range of δC^{13} (methane) suggests that the D-3 natural gases have been derived from marine source rocks in agreement with Deroo et al. (1977).

Four D-3 pools in Figure II - 37 fall off the main δC^{13} (methane) vs. $C_1/C_1 + C_2$ trend, outside the error of analysis ($\sigma\ \delta CH_4 = 0.2^o/oo$, $\sigma\ C_1/C_1 + C_2 = \pm 0.03$). These pools are Leduc Woodbend, Yekau Lake, Acheson and Clive. The oils in these pools have been classed as Group A oils (see Part II, Chapter II) which were interpreted to have been matured in deeper pools and migrated up dip to their present position after being displaced by gas. The carbon isotope composition of the methane from these four pools is too C^{13} - enriched compared to its $C_1/C_1 + C_2$ ratio versus the other D-3 samples.

The very uniform plot of δC^{13} (methane) vs. $C_1/C_1 + C_2$ suggests that up dip gas migration has either a very strong or very slight influence on the carbon isotope composition of methane and the bulk composition of D-3 natural gas. The latter opinion is preferred since only 4 pools (Clive, Yekau Lake, Leduc Woodbend and Acheson) are anomalous in their oil and gas chemistry. According to Alekseyev et al. (1972) the potential to fractionate the carbon isotopes of natural gas during migration does exist, primarily through the processes of diffusion, absorption, solution and degassing and phase transitions. However, in the opinion of Feux (1976) any migration fractionation effect should be observed mainly in the migrating front. Once the gas collects in the reservoir trap, successive migrating fronts will be more C^{13} - enriched producing an aggregate gas whose carbon isotope value is little different from premigration values. However, if a significant portion of the migrating gas is lost at some stage, then isotope differences could be observed in the pools along the migration route. If diffusion migration is an important carbon isotope fractionation process, then the task of sorting maturation effects from migration effects becomes quite difficult. And, the use of δC^{13} values of the methane, ethane and propane components as a geochemical index would be of dubious value.

The carbon isotope composition of the ethane and propane gas components have been plotted versus the $C_1/C_1 + C_2$ ratio in Figures II - 38 and II - 39 respectively. The ethane and propane plots show diminishing C^{12} contents with increasing $C_1/C_1 + C_2$ ratios as does the methane data in Figure II - 37. However, unlike the methane plot which shows one continuous function, the ethane and propane data discriminate between the Homeglen-Rimbey-Redwater and the grouped Wimborne-Duhamel and Stettler-West Drumheller associated gases. The best separation is achieved using the ethane versus $C_1/C_1 + C_2$ plot. It is worthwhile to speculate on the reason for the δC^{13} and $C_1/C_1 + C_2$ data for ethane and propane being able to discriminate between D-3 hydrodynamic systems while methane does not. Provided that all three gas components were generated in the source over the same period of time, then their migration paths from the source to the reservoir should be the same within any one system. It is possible that the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller hydrodynamic systems have migration paths whose lengths and fractionation capabilities are different. As a result, a plot of parameters such as the carbon isotope value of a gas component versus a gas bulk composition factor such as the $C_1/C_1 + C_2$ ratio should show the effects of the different migration paths. However, if migration fractionation were an important factor, methane should be increasingly more abundant the further a pool is along the migration path. The $C_1/C_1 + C_2$ ratio

FIGURE II-38

PLOT OF THE CARBON ISOTOPE COMPOSITION OF ETHANE vs $C_1/C_1 + C_2$

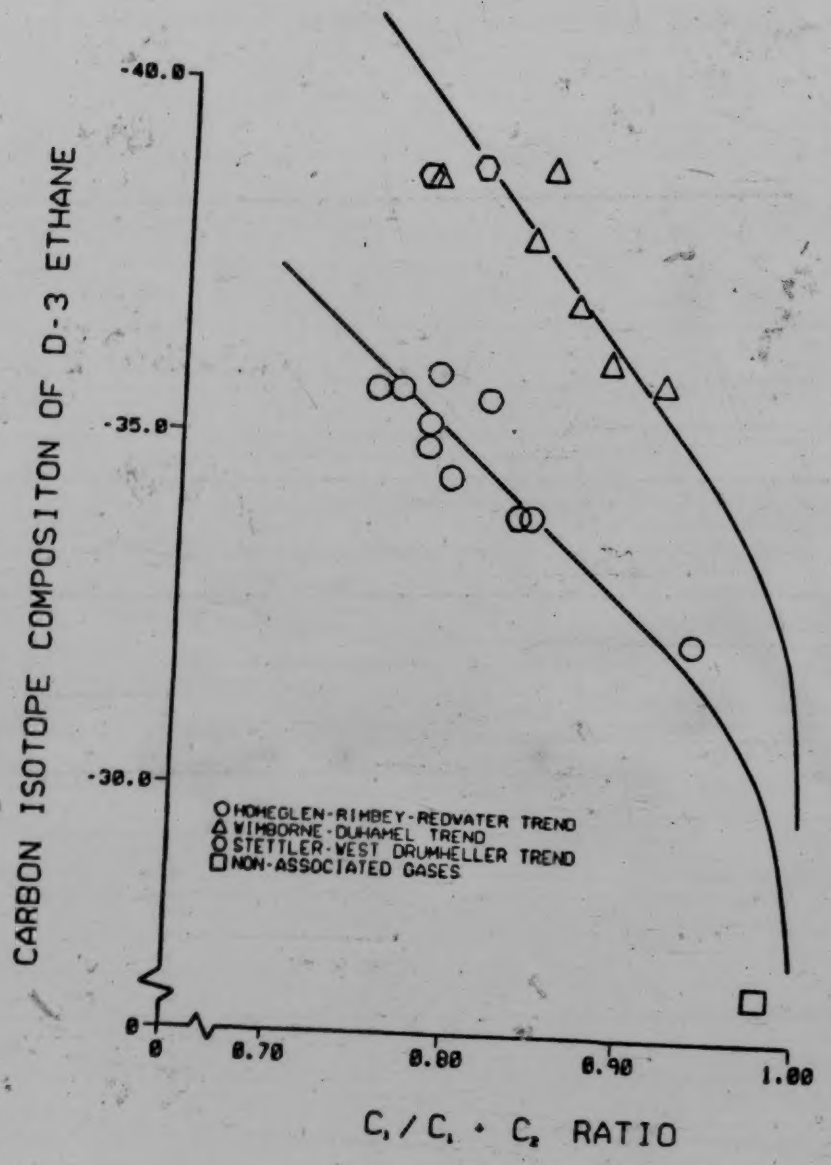
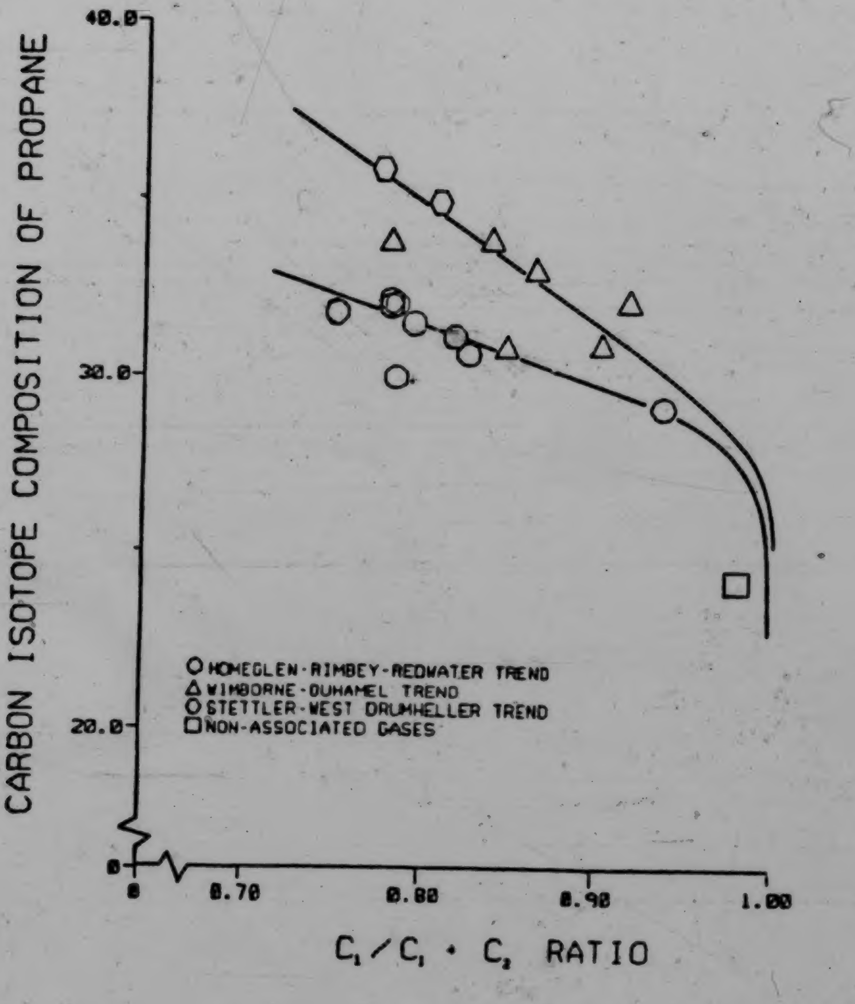


FIGURE II - 39

PLOT OF THE CARBON ISOTOPE COMPOSITION OF PROPANE vs $C_1/C_1 \cdot C_2$



trend shows the exact opposite. One more point is worth noting, and that is, the Stettler-West Drumheller and Wimborne-Duhamel associated gases contain significantly more hydrogen sulphide than the associated gases from the Homeglen-Rimbey-Redwater hydrodynamic system. Consequently the oil sulphurization reaction and the hydrogen sulphide generation mechanism may be responsible for the discriminatory ability of ethane and propane in Figures II - 38 and II - 39. Methane could be predominantly a product of maturation, whereas significant quantities of ethane and propane could be produced by carboxylic acid formation, oil sulphur compound production and cyclization reactions resulting from oil - sulphur interactions and oil oxidation by sulphite and thiosulphate radicals. The author is aware of no experimental evidence to support this contention.

The trend shown in Figure II - 37, where the C^{13} content of methane increases as the natural gas becomes drier (increasing $C_1/C_1 + C_2$), is generally accepted to be the result of maturation (see Feux, 1977 and Stahl, 1977). The shape of this curve (excluding the Redwater and West Drumheller data) is similar to a closed system plot of Δ vs. f (see Part II, Chapter III). However Figure II - 37 is not a simple closed system plot conforming to the equation:

$$\delta C^{13}_{CH_4} = -1000 \frac{(1 - f)}{f} (1 - f)^{\frac{1}{\alpha} - 1} - 1 + \delta C^{13}_{source,\ t = 0}$$

where f is the fraction of source carbon converted to methane and α is the fractionation factor.

For example, $C_1/C_1 + C_2$ is only proportional to f (the fraction of organic matter converted to methane) and the proportionality relationship is virtually undefinable due to the many side reactions which produce intermediate organic compounds when the source (kerogen or oil) is matured. Each of these intermediate compounds is thermodynamically unstable compared to methane, but each compound contains a portion of the source carbon and has an isotope composition controlled by the total carbon released from the source material and the isotope fractionation factor(s) involved in the formation and destruction of the compound. Furthermore, α, the fractionation factor varies quite markedly with temperature (Frank and Sackett, 1969). And, α is dependent on the parent organic carbon composition and its extent of thermal degradation (see Sackett, 1968; Sackett _et al_. 1968 and Frank _et al_. 1974).

The isotope composition of methane may be controlled in part by an equilibrium with carbon dioxide. Methane carbon is, on the average, 33* times more abundant than carbon dioxide carbon in the D-3 pools studied, except for the Stettler and West Drumheller gases which contain more carbon dioxide by a factor of about 7. If all the carbon dioxide in the D-3 natural gases were derived from marine limestone, whose average δC^{13}_{PDB} is 0.0^{o}/oo, and if this were mixed and equilibrated with average D-3 methane, whose δC^{13} value is -44.5^{o}/oo, then methane would become more enriched in C^{12} by 0.1^{o}/oo and carbon dioxide would become more enriched in C^{13} by 3.4^{o}/oo at 100°C (refer to Ohmoto, 1972 and Bottinga, 1969). As a result methane - carbon dioxide isotope exchange equilibria would produce only a slight effect on the isotope composition of methane. Furthermore, as reported by Bottinga (1969), it cannot be conclusively demonstrated that low temperature methane - carbon dioxide equilibria occur. The isotope composition of D-3 methane is probably the result of kinetic isotope effects associated with the thermal cracking of the carbon source together with a closed system or partially closed system isotope effect which relates the carbon del value of the product to the fraction of source material cracked. Mixing of methane generated from the *in situ* thermal cracking of oil with methane migrating up dip from deeper source beds would also have some control on the isotope composition of this gas. Presumably the deviation of the methanes from the Leduc Woodbend, Yekau Lake, Acheson and Clive D-3 pools from the main plot in Figure II - 37 is a result of this latter mixing process.

---

*This figure is based on gas analyses provided by the Energy Resources Conservation Board, White (1960) and Larson (1969).

In Figures II - 40, II - 41 and II - 42 the difference in isotope

FIGURE II - 40
PLOT OF δC^{13} (METHANE) - δC^{13} (ETHANE) vs
$C_1/C_1 + C_2$ RATIO

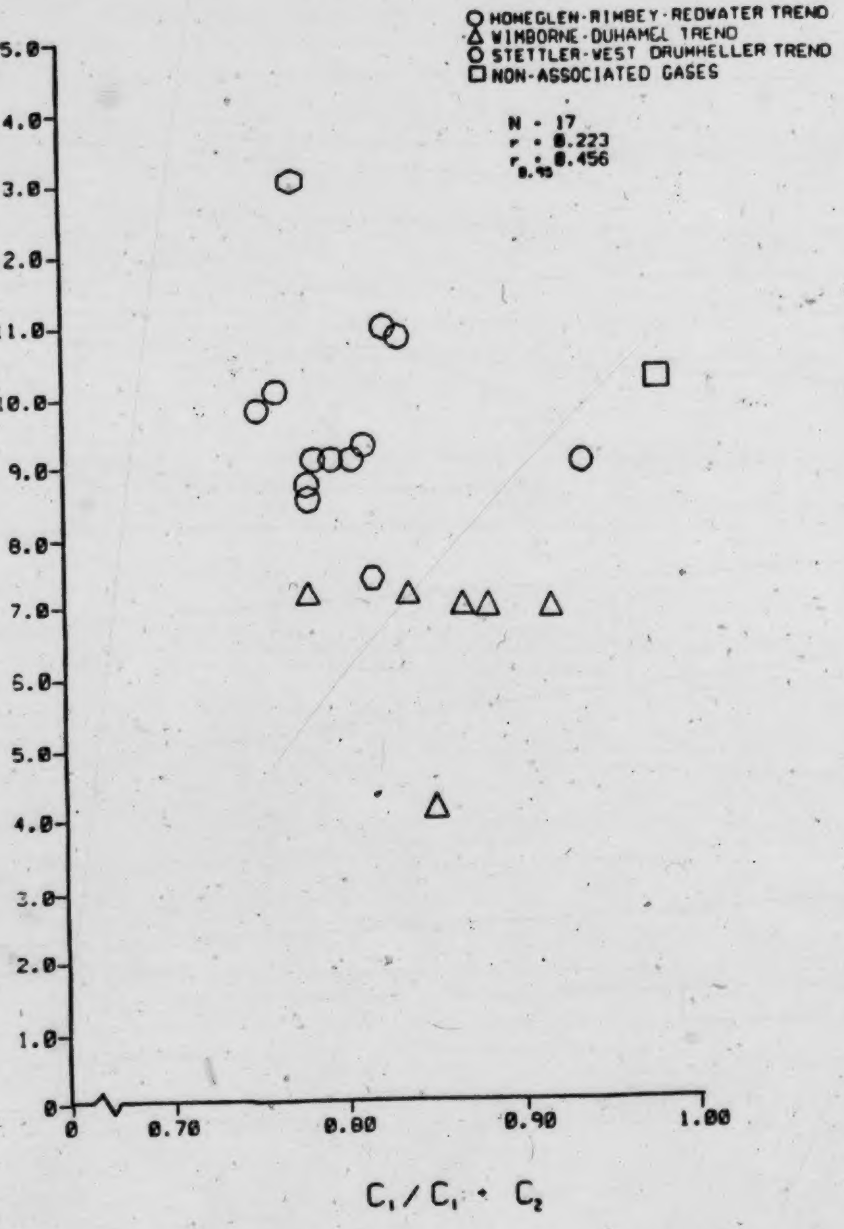


FIGURE II-41

PLOT OF δC^{13}(METHANE)-δC^{13}(PROPANE) vs $C_1/C_1 + C_2$

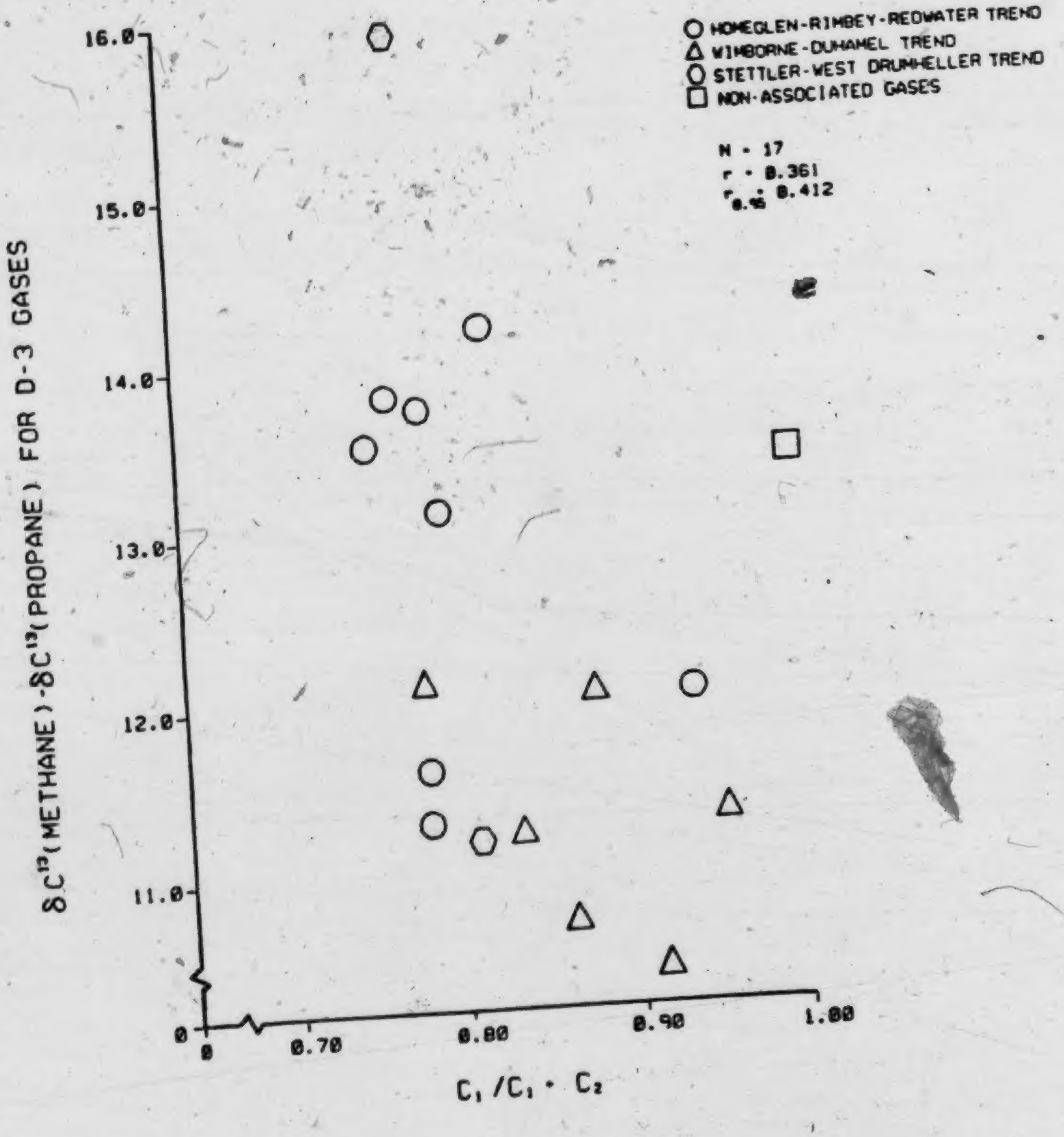
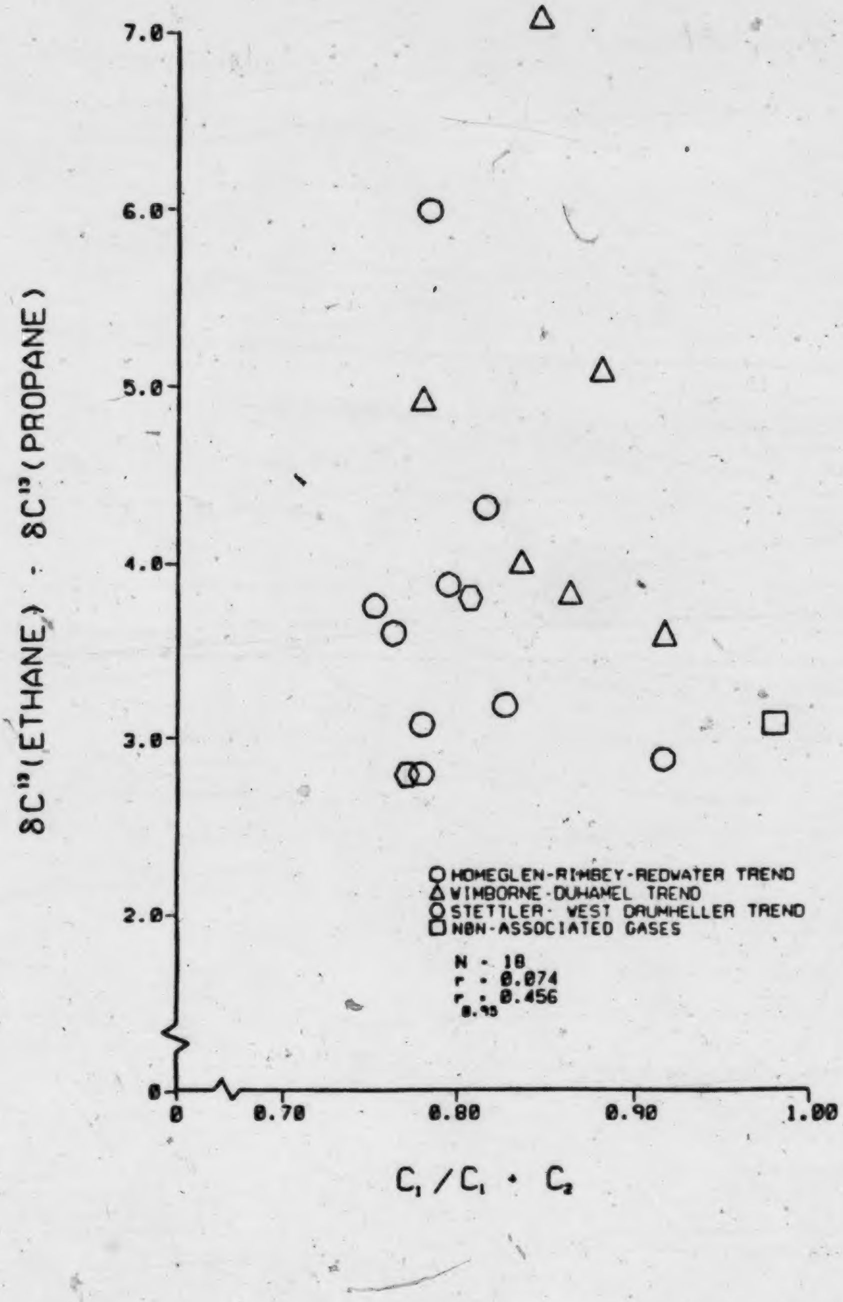


FIGURE II - 42

PLOT OF δC^{13} (ETHANE) - δC^{13} (PROPANE) vs $C_1/C_1 \cdot C_2$



composition between methane and ethane, methane and propane and ethane and propane have been plotted versus the $C_1/C_1 + C_2$ ratio. There is no correlation between the carbon isotope differences and the $C_1/C_1 + C_2$ ratio for either the total data distributions or data plotted as the hydrodynamic systems. Therefore, there may be no relationship at all between the generation of methane, ethane and propane. This is unlikely since all three are products of the thermal cracking of more complex hydrocarbons. The independence of the carbon isotope differences probably results from the complex interrelationship of the various isotope fractionation effects that are involved in the numerous side reactions of the thermal maturation process. It is unlikely that such a system could be described by a simple difference of two variables plotted against a maturation parameter.

In Part II, Chapter II the relationship of the C^{12} content of the D-3 oils, and of the saturate and aromatic fractions to the degree of maturation, was found to be an increasing C^{12} content with increasing maturation. This trend was noted to be the reverse of the theoretical relationship defined by Silverman (1964) which has been supported by data from Orr (1974). In Figures II - 43 and II - 44 the pool average carbon isotope values of methane have been plotted versus the pool average carbon isotope values for the whole oil and aromatic fraction respectively. In both figures, δC^{13} (methane) shows a significant negative linear relationship to the carbon isotope value of the related oil and oil fraction for the Homeglen-Rimbey-Redwater pools. Not

FIGURE II-43

PLOT OF δC^{13} (WHOLE OIL) vs δC^{13} (METHANE) FOR D-3 OILS AND GASES

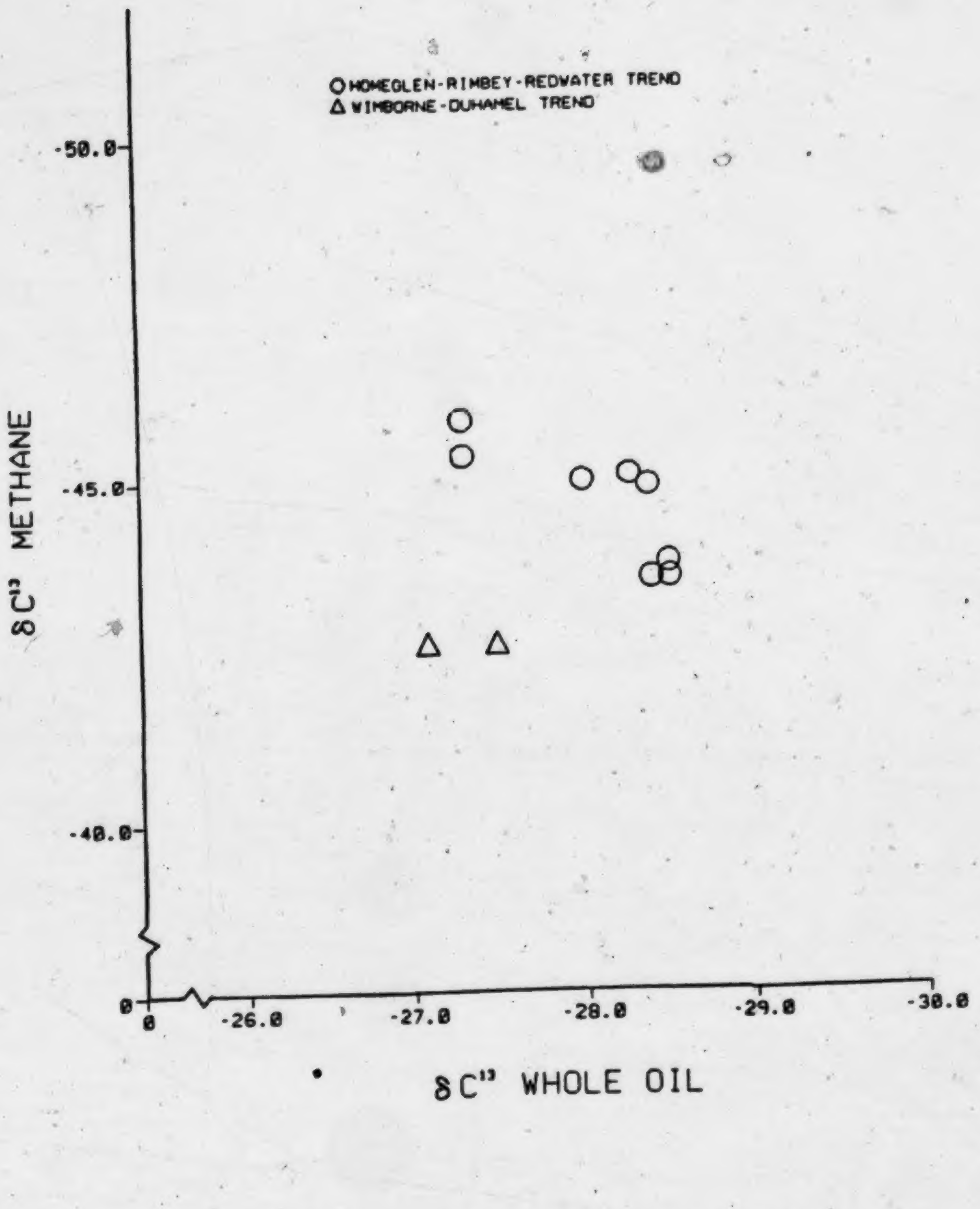
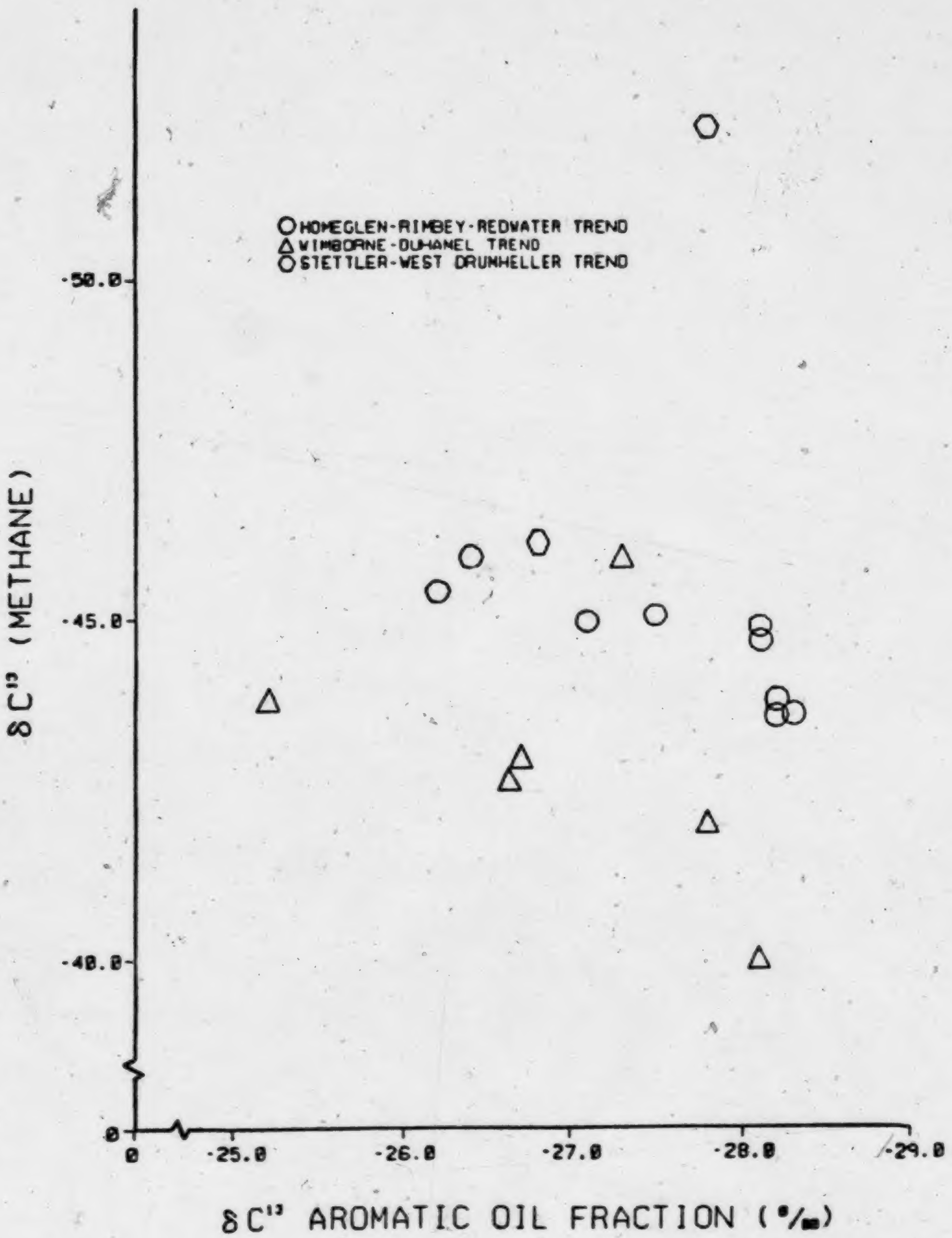


FIGURE II-44

PLOT OF δC^{13} (AROMATICS) vs δC^{13} (METHANE) FOR D-3 OILS AND GASES



enough data are available to assess the methane - whole oil relationship for the Stettler-West Drumheller and Wimborne-Duhamel trends. The Wimborne-Duhamel system, with the exception of the New Norway pool, shows a negative curvilinear relationship between the carbon isotope value of methane and the δC^{13} value of the aromatic oil fraction. If these relationships are the result of cause and effect, then the oil and aromatic fraction increases their C^{12} content at the expense of the associated methane gas component. The carbon isotope value of ethane shows a similar negative relationship only in the Homeglen-Rimbey-Redwater system (refer to Figure II - 45).

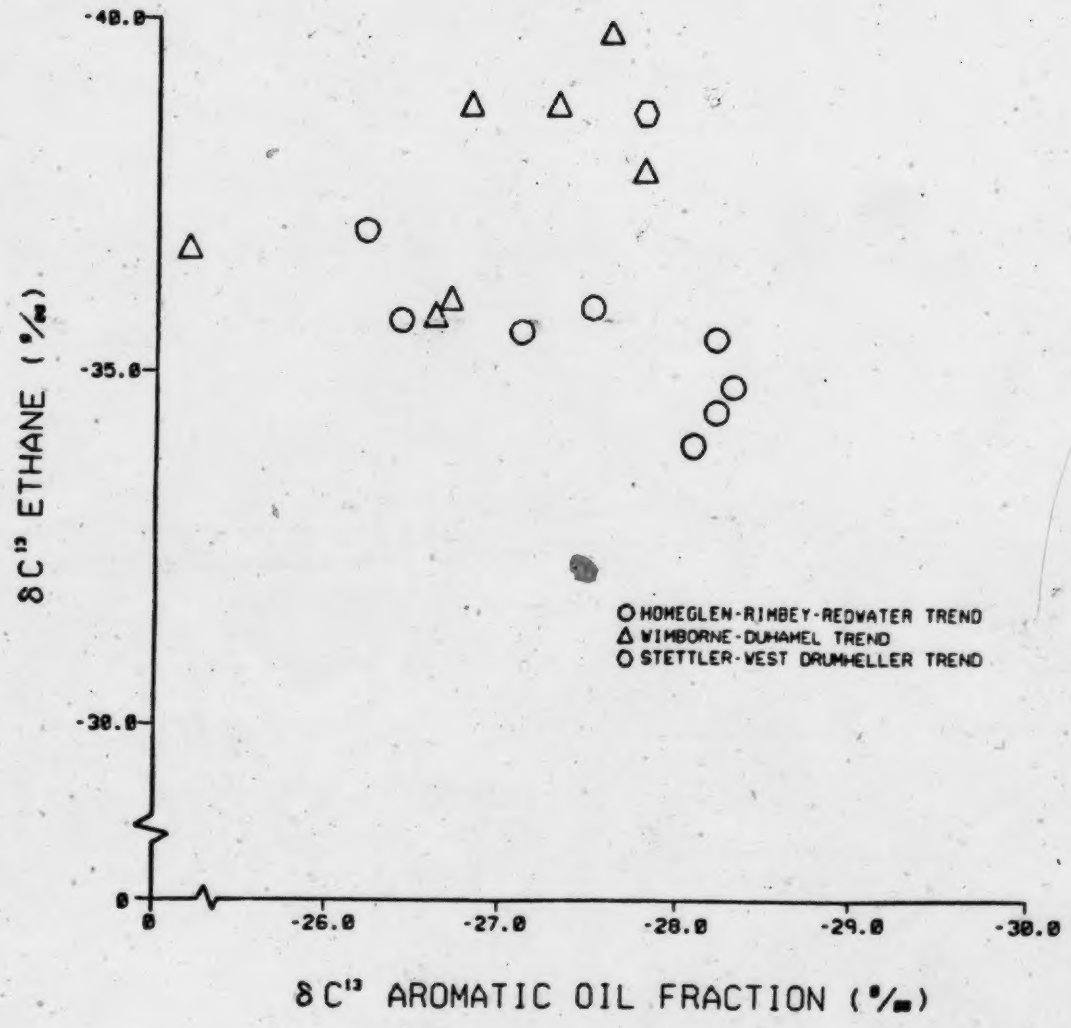
These negative isotope correlations could have been produced by a closed system isotope effect with a variable fractionation factor (α). Frank and Sackett (1969) calculated kinetic carbon isotope fractionation factors for the pyrolysis of neopentane. At temperatures near 100°C α is around 1.100, and it declines to values near 1.030 at temperatures in excess of 300°C. If such large variations in α^{+} occur during the maturation of a liquid as complex as crude oil then the negative relationship between the carbon isotope value of methane and crude oil can be understood. Consider the simple model where neopentane is pyrolysed to methane, and no long-lived reaction intermediates are produced. The difference (Δ) between the initial δC^{13} value of neopentane and its carbon isotope composition at some later stage during the pyrolysis is given by the equation:

$$\Delta = (f\alpha^{-1} - 1)1000$$

[+] Here α is only an average value which describes the overall behavior of the system.

FIGURE II-45

PLOT OF δC^{13} (AROMATICS) vs δC^{13} (ETHANE) FOR D-3 OILS AND SOLUTION GASES



Where f is the amount of unpyrolysed neopentane. The difference in the isotope composition of methane and the δC^{13} value of the initial neopentane is related to f through the following equation:

$$\Delta = -1000 \frac{f}{1 - f} \quad f^{\frac{1}{\alpha} - 1} - 1$$

In Figure II - 46 the logarithm of the absolute value of Δ (methane) and Δ (neopentane) for $\alpha = 1.100$, 1.060 and 1.030 have been plotted versus f. Δ (methane) values are negative, but have been considered as a positive quantity to facilitate the logarithmic transform. In Figure II - 47 Δ (methane) has been plotted versus Δ (neopentane) for f (0.70, 0.60, 0.40) and α(1.100, 1.060, 1.030). For this particular case, as f and α decreased with increasing intensity of maturation, the carbon isotope composition of the liquid became more C^{12} - enriched as the gas became more C^{13} - enriched. A similar carbon isotope trend is observed in the D-3 for the Homeglen-Rimbey-Redwater reef pools.

In Part II, Chapter II, Section 3 of this thesis, the trend of increasing C^{12} content of the oil with increasing degree of maturation was explained on the basis of gas deasphalting. In this section, it has been demonstrated that such a relationship could be produced by the in situ closed system thermal decomposition of an oil pool. Depending on the probability that is assigned to the existence of a natural closed system and on the likelihood that α varies significantly with

FIGURE II-46

PLOT OF LOG |Δ| vs f FOR THE PYROLYSIS OF NEOPENTANE

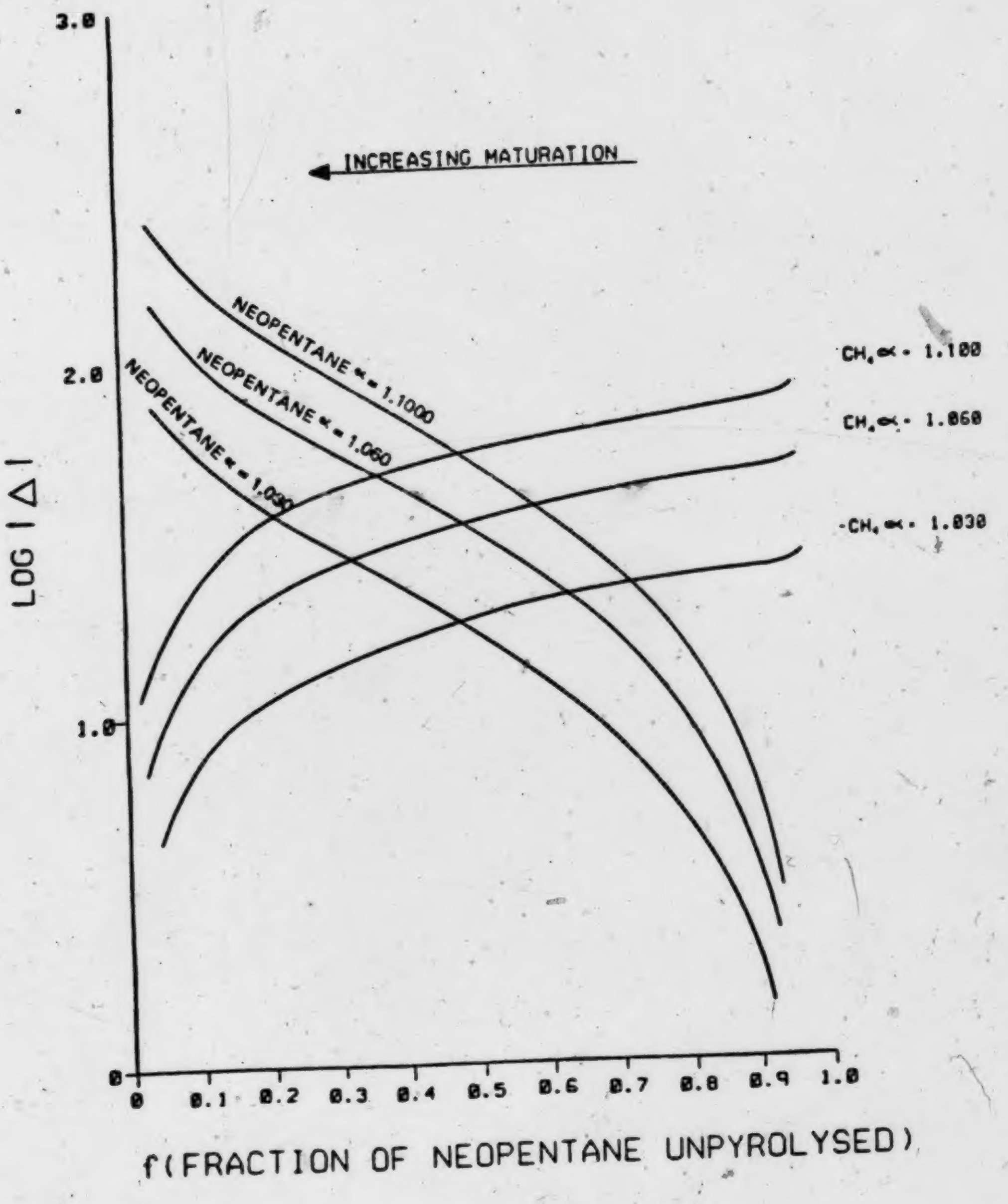
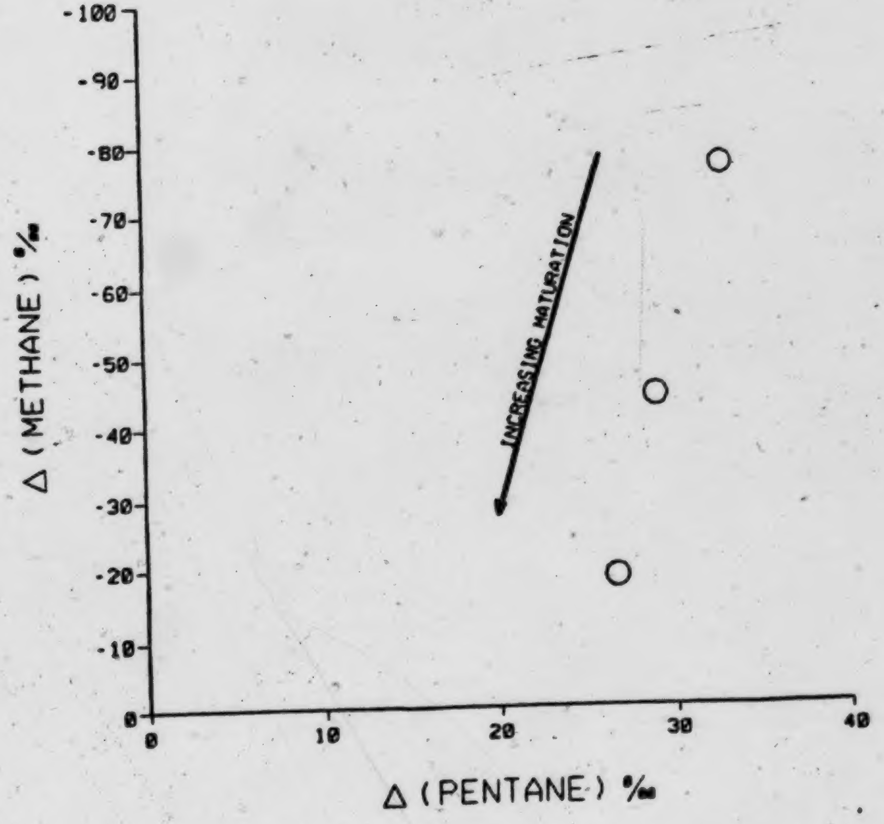


FIGURE II - 47

PLOT OF Δ METHANE vs Δ PENTANE

r	Δ CH_4	Δ PENTANE	α
0.70	-77	·33	1.100
0.60	-44	·29	1.060
0.40	-18	·27	1.030



temperature, one model or the other may be preferred.[+] The closed system model provides an interrelated explanation for the behavior of the carbon isotopes of the oil and gas phases. But of necessity, it rejects any additions or losses of oil or gas after the oil pool is formed (the system is closed). In reality oil and gas accumulation in the D-3 is a continuing process, accented by major phases of generation and accumulation. Therefore, the concept of a quasi-closed system is preferred, in which only very minor contents of oil and gas are added to the pools after the main phase of hydrocarbon generation and migration. The mathematics of the closed system only approximate the behavior of the quasi-closed system but the approximation should be close enough to indicate general trends. The very simple neopentane model demonstrates that in a series of closed systems which undergo progressive maturation, the liquid phase can become more C^{12} - enriched as the gaseous phase is enriched in C^{13}. An analogous system may exist in the D-3 reservoir.

[+] Deasphalting a crude oil has the effect of decreasing its carbon del value by removing compounds enriched in C^{13}. On the otherhand, methane generation, a natural consequence of maturation, removes C^{12} from the oil and therefore increases the carbon del value of the oil. Which process (deasphalting or methane generation) has the greatest control over the carbon isotope composition of the oil during maturation is the crux of the argument for a closed system model versus a deasphalting model. Dr. C. R. Evans (personal communication) considers deasphalting to be an important influence on the composition of an oil and therefore believes that this observed C^{12} enrichment of an oil with increasing maturity results from deasphalting.

CONCLUSIONS

1) Oil fraction (saturate, aromatic, maltene, NSO) and oil sulphur abundances are effected markedly by data closure.

2) A Q-mode factor analysis of oil sulphur percentages and oil fraction data for Leduc and Keg River oils identifies two main processes which affect the composition of the oils: maturation and sulphurization.

3) A graph of Factor I loadings versus present day reservoir temperature defines three groups of Leduc oils which have been designated as Groups A, B, C. Group B oils can be interpreted as oils whose composition is mainly controlled by maturation. Group C oils can be interpreted as oils whose composition is controlled mainly by sulphurization. Group A oils are essentially Group B oils which have been displaced up-dip from deeper, hotter, reservoirs by migrating gas.

4) Gas-liquid chromatography of the saturate oil fraction for the Leduc and Keg River oils shows no evidence that these oils have been biodegraded.

5) Leduc oils from the Homeglen-Rimbey-Redwater, Wimborne-Duhamel and Stettler-West Drumheller reef trends probably form one oil family.

6) The mean and range of carbon isotope analyses (respectively $-28^{o}/oo$ and -27.2 to $-28.7^{o}/oo$) for oils from the Leduc and Keg River formations indicate that these oils have been generated from marine source rocks of Devonian age.

7) δC^{13} analyses of Leduc oils and their saturate and aromatic fractions, indicate a significant enrichment in C^{12} with increasing maturation. This C^{12} enrichment trend is contrary to the accepted trend of increasing C^{13} content as the oils become increasingly more mature.

8) The carbon isotope values for the Keg River and Leduc oils overlap to such an extent that the two isotope populations are indistinguishable. Furthermore, a plot of δC^{13} (aromatics) versus δC^{13} (saturates) does not discriminate between Keg River and D-3 oils. Therefore, either the Keg River and Leduc oils have very similar source organic matter, or carbon isotopes are not suited to some oil correlation problems.

9) Carbon isotope values for the methane, ethane and propane paraffin homologs are more C^{12} enriched than their associated oils.

10) The trend δC^{13} (methane) < δC^{13} (ethane) < δC^{13} (propane) was observed for every Leduc and Keg River natural gas analysed.

11) A plot of δC^{13} (methane) versus the $C_1/C_1 + C_2$ ratio defines a continuous curve which has a marked slope reversal at a carbon del value of about - 46°/oo. This slope reversal suggests that there are two fundamentally different thermochemical methane generation reactions.

12) Two classes of Leduc hydrocarbons can be recognized from δC^{13} (methane) values. These are mature and overmature (metamorphosed).

13) The range of carbon del values together with the continuous curve defined by the δC^{13} (methane) versus $C_1/C_1 + C_2$ ratio suggests that the D-3 natural gases have been derived from marine source rocks.

14) The effects of migration isotope fractionation on the carbon isotope values of D-3 natural gases cannot be easily assessed. However, plots of δC^{13} (ethane) and δC^{13} (propane) versus the $C_1/C_1 + C_2$ ratio discriminate the Homeglen-Rimbey-Redwater trend gases from the natural gases of the other two Leduc hydrodynamic systems. This discrimination may result from fractionation during migration.

15) There is no correlation of the difference between the carbon isotope composition of methane and ethane; ethane and propane; and methane and propane with the $C_1/C_1 + C_2$ ratio. This probably results from the complex and irreversible nature of the maturation reaction.

16) The observed trends of C^{13} enrichment in methane and C^{12} enrichment of the associated oil, and oil fraction with increasing maturity, can be explained using a closed system maturation - isotope fractionation model.

17) Leduc Group B' and Group C oils have a statistically significant negative linear correlation between δS^{34} (oil) and Factor I loadings. As a result, the variation in the sulphur isotope composition of oil sulphur is probably controlled by maturation and sulphurization reactions.

18) Oils from the same family can have a wide range (14°/oo) in sulphur isotope composition.

19) Due to the statistically significant relationships between δS^{34} (oil) vs. maturation; and δC^{13} (oil), δC^{13} (saturates) and δC^{13} (aromatics), vs. maturation, it is necessary to define oil families and their isotope variation and then correlate between the families, not between the individual oils.

20) Sulphur isotope values from oil and solution gas samples indicate that the sulphur source for the Leduc and Keg River pools is different.

21) The difference between the mean δS^{34} values for Keg River and Leduc solution gas (-8.4^{o}/oo) is quite similar to the difference between the mean sulphur del values for Middle Devonian and Upper Devonian evaporites (-7.0^{o}/oo). This relationship supports the accepted opinion that evaporites associated with the oils and gases are the sulphur source.

22) Both the magnitude and direction of sulphur isotope enrichment for co-produced D-3 sulphur samples is compatible with an equilibrium isotope exchange reaction with hydrogen sulphide.

23) The significant linear correlation between the sulphur del values of reactive gaseous sulphide (primarily H_2S) and present day reservoir temperature can be explained using a closed system sulphate reduction model.

24) Hydrogen sulphide in the Leduc reservoir system is believed to be produced by the reduction of Upper Devonian sulphate (lining the vugs and pore spaces of D-3 pools) through Toland type chemical reactions.

25) The Toland reaction can explain the oxidation of an overmature dry gas deposit to an accumulation of elemental sulphur, hydrogen sulphide, sulphanes and carbon dioxide.

26) Although the Toland reaction cannot be conclusively demonstrated as responsible for the production of major amounts of hydrogen sulphide and sulphur compounds in the D-3 reservoir system, this reaction forms a redox couple which (over geologic time) has the potential to generate an abundance of sulphur compounds over a fairly wide range of reservoir temperature. The reaction is self sustaining and can establish its own favorable chemical environment through sulphide equilibria.

Closed systems (meant in the mathematical and the chemical-Rayleigh sense) appear to have a marked effect on the variation in the composition of the Devonian Leduc oils and natural gases. Isotope models based on the closed system explain the variation in the sulphur isotope composition of reactive gaseous sulphide and the general variation in the carbon isotope composition of the Leduc oils and associated natural gases. Also, much of the variation in Leduc oil fraction percentages may be due to changes in only the saturate content and data closure.

It is important to recognize the effects of mathematical and chemical closure on information from any geochemical system. Once this is done, genuine variations in the geochemical information from a system can be identified with probable chemical processes.

REFERENCES

Alekseyev, F. A., V. S. Lebedev and T. A. Krylova (1973). Isotope Composition of Carbon in Gaseous Hydrocarbons and Conditions for Accumulations of Natural Gas: Internat. Geol. Rev., V. 15, No. 3, p. 300-308.

Bailey, N. J. L., A. M. Jobson, and M. A. Rogers (1973). Bacterial Degradation of Crude Oil - Comparison of Field and Experimental Data: Chemical Geology, V. 11, p. 203-221.

Baird, D. C. (1962). Experimentation - An Introduction to Measurement Theory and Experiment Design: Prentice-Hall Inc., 198 p.

Baker, E. G. (1967). A Geochemical Evaluation of Petroleum Migration and Accumulation: in Fundamental Aspects of Petroleum Geochemistry; B. Nagy and U. Colombo (editors); Elsevier, New York.

Barghoorn, E. S., W. G. Meinschein and J. W. Schopf (1965). Paleobiology of a Precambrian Shale: Science, V. 148, p. 461-472.

Barrow, G. M. (1966). Physical Chemistry (2nd Edition): McGraw-Hill, 843 p.

Berner, R. A. (1962). Tetragonal Iron Sulphide: Science, V. 137, p. 669.

Berner, R. A. (1963). Electrode Studies of Hydrogen Sulphide in Marine Sediments: Geochim. et Cosmochim. Acta, V. 27, p. 563-575.

Berner, R. A. (1964). Iron Sulphides Formed from Aqueous Solution at Low Temperatures and Atmospheric Pressure: Jour. of Geol., V. 72, p. 293.

Berner, R. A. (1967). Thermodynamic Stability of Sedimentary Iron Sulphides: Am. Jour. Sci., V. 265, p. 773-785.

Berner, R. A. (1969). Migration of Iron and Sulphur within Anaerobic Sediments During Early Diagenesis: Am. Jour. Sci., V. 267, p. 19-42.

Berner, R. A. (1970). Sedimentary Pyrite Formation: Am. Jour. Sci., V. 268, p. 1-23.

Berner, R. A. (1971). Principles of Chemical Sedimentology: McGraw-Hill, 240 p.

Bestougeff, M. A. and D. Jolly (1967). Separation et Identification des Composes Soufres a Haut Poids Moleculaire Dans les Petroles: Proc. Seventh World Pet. Cong., V. 9, p. 129-147.

Bestougeff, M. A. (1973). Introduction a la Session: Le Soufre dans les Combustibles Fossiles et dans les Sediments: *in* Advances in Organic Geochemistry; editors B. Tissot, and F. Bienner, Editions Technip, Paris, p. 725-726.

Bestougeff, M. A. and A. Combaz (1973). Action d'H_2S et de S sur Quelques Substances Organiques Actuelles et Fossiles: *in* Advances in Organic Geochemistry; B. Tissot and F. Bienner (editors), Editions Technip, Paris, p. 747-759.

Biederman, E. W. (1975). Time of Hydrocarbon Expulsion, Paradox for Geologists and Geochemists: discussion, Am. Assoc. Pet. Geol., V. 59, p. 2050-2053.

Bigeleisen, J. (1949). The Relative Reaction Velocities of Isotopic Molecules: Jour. Chem. Phys., V. 17, p. 675-678.

Bottinga, Y. (1969). Calculated Fractionation Factors for Carbon and Hydrogen Isotope Exchange in the System Calcite - Carbon dioxide - Graphite - Methane - Hydrogen - Water Vapor: Geochim. et Cosmochim. Acta, V. 32, p. 49-64.

Boulegue, J. (1973). Etude Experimentale du Comportement du Soufre dans les Milieux Marins Oxydants et Reducteurs Consequences pour la Matiere Organique: *in* Advances in Organic Geochemistry; editors B. Tissot and F. Bienner, Editions Technip, Paris, p. 813-827.

Broecker, W. S. and V. M. Oversby (1971). Chemical Equilibria in the Earth: McGraw-Hill, 318 p.

Burnie, S. W. (1975). A Sulphur Study of Sour Gases Sampled from Several D-3 Pools Within the Upper Devonian of Alberta, Canada: Abstract; AAPG - SEPM Annual Convention, Dallas, Texas, 1975.

Burns, B. J., J. T. C. Hogarth, and C. W. D. Milner (1975). Properties of Beaufort Basin Liquid Hydrocarbons: Bull. Can. Pet. Geol., V. 23, p. 295-303.

Calvin *et al*. (1949). Isotopic Carbon: John Wiley and Sons Inc. U.S.A.

Century, J. R. (1966). Oil Fields of Alberta Supplement: J. R. Century (editor), pub. by Alta. Soc. Pet. Geol., 136 p.

Chayes, F. (1960). On Correlation between Variables of Constant Sum: Jour. Geophys. Res., V. 65, No. 12, p. 4185-4193.

Chayes, F. (1962). Numerical Correlation and Petrographic Variation: Jour. Geol., V. 70, No. 4, p. 440-452.

Chayes, F. (1970). Effect of a Single Non-zero Open Covariance on the Simple Closure Test: in Geostatistics, Plenum Press, New York, p. 11-22.

Clark, L. M. (1954). Western Canada Sedimentary Basin - A Symposium: published by Am. Assoc. Pet. Geol.; 521 p.

Coleman, M. L. and J. Gray (1972). An Adjustable Gas Inlet System for an Isotope Mass Spectrometer: The Review of Scientific Instruments, V. 43, No. 10, p. 1500-1503.

Colombo, U., and F. Gazzarini, G. Sironi, R. Gonfiantini and E. Tongiorgi (1966). Measurements of Carbon Isotope Ratios on Italian Natural Gases and Their Geochemical Interpretation: in Advances in Organic Geochemistry; G. D. Hodgson and M. C. Louis (editors), Pergamon Press, Oxford, p. 279-292.

Colombo, U. F. Gazzarini, R. Gonfiantin, E. Tongiorgi and L. Caflisch (1969). Carbon Isotope Study of Hydrocarbons in Italian Natural Gases: in Advances in Organic Geochemistry; P. A. Schenk and I. Havenaar (editors), Pergamon Press, Oxford, p. 499-516.

Connan, J. (1974). Time-Temperature Relation in Oil Genesis: Am. Assoc. Pet. Geol., V. 58, p. 2516-2521.

Craig, H. (1953). The Geochemistry of the Stable Carbon Isotopes: Geochim. et Cosmochim. Acta, V. 3, p. 53.

Craig, H. (1957). Isotopic Standards for Carbon and Oxygen, and Correction Factors for Mass-Spectrometric Analysis of Carbon Dioxide: Geochim. et Cosmochim. Acta, V. 12, p. 133-149.

Davies, G. R. (1975). Devonian Reef Complexes of Canada II: Can. Soc. Pet. Geol., Reprint Series No. 1; G. R. Davies (editor), published by the Can. Soc. Pet. Geol.; 246 p.

Dean, R. A. and E. V. Whitehead (1967). Status of Work in Separation and Identification of Sulphur Compounds in Petroleum and Shale Oil: Proc. Seventh World Pet. Cong., V. 9, p. 165.

Degens, E. T. (1969). Biogeochemistry of Stable Carbon Isotopes: in Organic Geochemistry; G. Eglington and M. T. J. Murphy (editors), Springer-Verlag, New York; p. 304-329.

Deines, P. (1970). Mass Spectrometer Correction Factors for the Determination of Small Isotopic Composition Variations of Carbon and Oxygen: Int. Jour. Mass Spectrom. Ion Phys., V. 4, p. 283-295.

Deroo, G., T. G. Powell, B. Tissot, R. G. McCrossan with contributions by P. A. Hacquebard (1977). The Origin and Migration of Petroleum in the Western Canadian Sedimentary Basin, Alberta - A Geochemical and Thermal Maturation Study: Geol. Survey of Canada Bulletin #262, 136 p.

Dhannoun, H. Y. and W. S. Fyfe (1972). Reaction Rates of Hydrocarbon with Sulphate: N. E. R. C. Publication, Series D. (Progress in Experimental Petrology), V. 2, p. 69-71.

Dixon, W. J. and F. J. Massey, JR. (1969). Introduction to Statistical Analysis: McGraw-Hill, 638 p.

Drushel, H. V. (1970). Sulphur Compounds in Petroleum - Known and Unknown: Am. Chem. Soc. Div. Petroleum Chemistry, preprint 15, No. 2, p. C12-C42.

Eglington, G. and M. T. J. Murphy (1969). Organic Geochemistry - Methods and Results: Springer Verlag, New York; 828 p.

Erdman, J. G., and D. A. Morris (1974). Geochemical Correlation of Petroleum: Am. Assoc. Pet. Geol., V. 58, No. 11, p. 2326-2337.

Evans, C. R., M. A. Rogers and N. J. L. Bailey (1971). Evolution and Alteration of Petroleum in Western Canada: Chemical Geology, V. 8, No. 3, p. 147-170.

Evans, C. R. and F. L. Staplin (1971). Regional Facies of Organic Metamorphism: in Geochemical Exploration 1970, Can. Inst. Min. Metall., Spec. V. 11, R. W. Boyle and J. I. McGerrigle (editors), p. 517-520.

Feely, H. W. and J. L. Kulp (1957). Origin of Gulf Coast Salt Dome Sulphur Deposits: Am. Assoc., Pet. Geol. Bull., V. 41, p. 1802-1853.

Feux, A. N. (1977). The Use of Stable Carbon Isotopes in Hydrocarbon Exploration: Jour. Geochem. Expl., No. 7, p. 189-211.

Frank, D. J. and W. M. Sackett (1969). Kinetic Isotope Effects in the Thermal Cracking of Neopentane: Geochim. et Cosmochim. Acta, V. 33, p. 811-820.

Frank, D. J., J. R. Gormly, and W. M. Sackett (1974). Revaluation of Carbon-Isotope Compositions of Natural Methanes: Am. Assoc. Pet. Geol., V. 58, No. 11, p. 2319-2325.

Fritz, P., R. J. Drimmie and V. K. Nowicki (1974). Preparation of Sulphur Dioxide for Mass Spectrometer Analyses by Combustion of Sulphides with Copper Oxide: Analytical Chemistry, V. 46, No. 1, p. 164-166.

Galimov, E. M., A. A. Ivlev and N. G. Kuznetsova (1970). Carbon Isotope Composition of Gaseous Hydrocarbons in Petroleum and the Problem of Their Origin: Geochemistry International, V. 7, p. 594-603.

Galimov, E. M. (1973). Organic Geochemistry of Carbon Isotopes: in Advances in Organic Geochemistry: editors B. Tissot and F. Bienner, Editions Technip, Paris, p. 439-462.

Garlick, G. (1969). Oxygen: in Handbook of Geochemistry, Wedepohl (editor), Springer-Verlag, New York.

Garrels, R. M. and C. L. Christ (1965). Solutions, Minerals and Equilibria: Harper and Row, 450 p.

Gousseva, A. N. and L. A. Fainguerch (1973). La Formation des Petroles Soufres dans les Zones de l'Hypergenese Ancienne: in Advances in Organic Geochemistry; editors B. Tissot and F. Bienner, Editions Technip, Paris, p. 741-759.

Gransch, J. A. and J. Posthuma (1973). On the Origin of Sulphur in Crudes: in Advances in Organic Geochemistry; editors B. Tissot, and F. Bienner, Editions Technip, Paris, p. 726-739.

Gussow, W. C. (1954). Differential Entrapment of Oil and Gas - A Fundamental Principle: Am. Assoc. Pet. Geol. Bull., V. 38, No. 5, p. 816-853.

Harrison, A. G. and H. G. Thode (1957). The Kinetic Isotope Effect in the Chemical Reduction of Sulphate: Trans. Faraday Soc., V. 53, p. 1648-1651.

Harrison, A. G. and H. G. Thode (1958). Mechanism of the Bacterial Reduction of Sulphate from Isotope Fractionation Studies: Trans. Faraday Soc., V. 54, p. 82-84.

Harwood, R. J. (1973). Biodegradation of Oil: in The Geology of Fluids and Organic Matter in Sediments; Natl. Conference on Earth Sciences, Banff, Alberta, Apr. 30 to May 4, 1973; p. 149-156.

Helgeson, H. C. (1969). Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures: Am. Jour. Sci., V. 267, p. 729-804.

Hitchon, B. (1964). Formation Fluids: in Geological History of Western Canada; R. G. McCrossan and R. P. Glaister (editors), published by Alberta Society of Petroleum Geologists, p. 201-217.

Hitchon, B. (1968). Geochemistry of Natural Gas in Western Canada: Am. Assoc. Pet. Geol., Mem. No. 9, p. 1995-2025.

Hitchon, B. (1969a). Fluid Flow in the Western Canada Sedimentary Basin. 1. Effect of Topography: Water Resources Research, V. 5, No. 1, p. 186-195.

Hitchon, B. (1969b). Fluid Flow in the Western Canada Sedimentary Basin. 2. Effect of Geology: Water Resources Research, V. 5, No. 2, p. 460-469.

Hitchon, B. and I. Friedman (1969). Geochemistry and Origin of Formation Waters in the Western Canada Sedimentary Basin: Geochim. et Cosmochim. Acta, V. 33, p. 1321-1349.

Hitchon, B. (1971). Origin of Oil - Geological and Geochemical Constraints: in Advances in Chemistry Series, No. 103 - Origin and Refining of Petroleum, p. 30-66.

Hitchon, B., G. K. Billings and J. E. Klovan (1971). Geochemistry and Origin of Formation Waters in the Western Canada Sedimentary Basin - III. Factors Controlling Chemical Composition: Geochim. et Cosmochim. Acta, V. 35, p. 567-598.

Hitchon, B. and M. K. Horn (1974). Petroleum Indicators in Formation Waters from Alberta, Canada: Am. Assoc. Pet. Geol., V. 58, No. 3, p. 464-473.

Hitchon, B. and H. R. Krouse (1975). Stable Isotope Geochemistry of Natural Gases from Devonian Strata, Alberta, Canada: Oral presentation by H. R. Krouse to the O.G.D. Symposium - Organic Geochemistry of Natural Gases, G.S.A. Meeting, Salt Lake City, October, 1975, 30 p.

Ho, T. Y., M. A. Rogers, H. V. Drushel and C. B. Koons (1974). Evolution of Sulphur Compounds in Crude Oils: Am. Assoc. Pet. Geol., V. 58, no. 11, p. 2338-2348.

Hunt, J. M. (1973). Organic Geochemistry of the Marine Environment: in Advances in Organic Geochemistry; editors B. Tissot and F. Bienner, Editions Technip, Paris, p. 593-605.

Hunt, J. M. (1975). Is There a Geochemical Depth Limit for Hydrocarbons?: Petroleum Engineer, March Vol., p. 112.

Husain, S. A. (1967). Sulphur Isotope Exchange Reactions: Doctorate Thesis; The University of Alberta, Physics Department, Edmonton, Alberta; 130 p.

Husain, S. A. and H. R. Krouse (1976). Sulphur Isotope Effects During the Reaction of Sulphate with Hydrogen Sulphide: Proc. Internat. Conf. Stable Isotopes, Inst. of Nuc. Sci., D.S.I.R., L. Hutt, New Zealand.

Hyne, J. B. (1968). Sulphur Deposition in Sour Gas Wells: Alberta Sulphur Research Institute Quarterly Bulletin, V.V, No. 1, p. 1-20.

Imbrie, J. and E. G. Purdy (1962). Classification of Modern Bahamian Carbonate Sediments: Am. Assoc. Pet. Geol., Memoir 1, p. 253-272.

Jensen, M. L. (1962). Biogeochemistry of Sulphur Isotopes: Proc. of a National Sci. Foundation Symposium; M. L. Jensen (editor).

Jobson, A., F. D. Cook and D. W. S. Westlake (1972). Microbial Utilization of Crude Oil: Applied Microbiology, V. 23, No. 6, p. 1082-1089.

Jobson, A. M. (1976). Physiological Characterization of a Desulphovibrio sp. Isolated from Crude Oil: Ph.D. Thesis, Dept. Microbiology, Univ. of Alta; Edmonton, Alberta.

Johnson, N. L. and F. C. Leone (1964). Statistics and Experimental Design, Volume I: John Wiley and Sons Inc., 523 p.

Joreskog, K., J. E. Klovan and R. E. Reyment (1976). Geological Factor Analysis: Elsevier, Amsterdam, 178 p.

Kaplan, I. R., K. O. Emery and S. C. Rittenberg (1963). The Distribution and Isotopic Abundance of Sulphur in Recent Marine Sediments off So. California: Geochim. et Cosmochim. Acta, V. 27, p. 297-331.

Kemp, A. L. W. and H. G. Thode (1968). The Mechanism for the Bacterial Reduction of Sulphate and Sulphite from Isotope Fractionation Studies: Geochim. et Cosmochim. Acta, V. 32, p. 71-91.

Klovan, J. E. (1963). Facies Analysis of the Redwater Reef Complex, Alberta, Canada: Bul. Can. Pet. Geol., V. 12, No. 1, p. 1-100.

Klovan, J. E. and J. Imbrie (1971). An Algorithm and FORTRAN - IV Program for Large-Scale Q-mode Factor Analysis and Calculation of Factor Scores: Jour. Math. Geol., V. 3, No. 1, p. 61-67.

Koons, C. B., J. G. Bond and F. L. Peirce (1974). Effects of Depositional and Post Depositional History on Chemical Composition of Lower Tuscaloosa Oils: Am. Assoc. Pet. Geol. Bull., V. 58, p. 1272-1280.

Krauskopf, K. (1967). Introduction to Geochemistry: McGraw-Hill, 721 p.

Krouse, H. R. (1977). Sulphur Isotope Studies and Their Role in Petroleum Exploration: Journal of Geochemical Exploration, No. 7, p. 189-211.

Larson, L. H. (1969). Gas Fields of Alberta: L. H. Larson (editor), pub. by Alta. Soc. Pet. Geol., 407 p.

LeTran, K. (1971). Geochemical Study of Hydrogen Sulphide Sorbed in Sediments: in Advances in Organic Geochemistry, Pergamon Press, p. 717-726.

LeTran, K., J. Connan and B. Van Der Weide (1973). Problemes Relatifs a la Formation d'Hydrocarbures et d'Hydrogene Sulfure dans le Bassin Sud-Ouest Aquitain: in Advances in Organic Geochemistry; editors B. Tissot and F. Bienner, Editions Technip, Paris, p. 761-789.

Levorsen, A. I. (1967). Geology of Petroleum: W. H. Freeman and Company, 724 p.

Marzec, A., H. Kozikowski, J. Glogoczowski and W. Kisielow (1971). Problems of Migration of Polish Crude Oils on the Basis of Geochemical Correlation Data and Carbon Isotope Composition: Chemical Geology, V. 8, No. 3, p. 197-217.

Maxwell, J. A. (1968). Rock and Mineral Analysis: John Wiley and Sons.

McCrossan, R. G. and R. P. Glaister (1964). Geological History of Western Canada: R. G. McCrossan and R. P. Glaister (editors) pub. by Alta. Soc. Pet. Geol., 232 p.

McNab, J. G., P. V. Smith, JR. and R. L. Betts (1952). The Evolution of Petroleum: Industrial and Engineering Chemistry, V. 44, No. 11, p. 2556-2563.

Mehmet, Y. (1971). The Occurrence and Origins of Sulphur Compounds in Crude Oils - A Review: Alberta Sulphur Research Ltd., V. VIII, No. 1, p. 1-18.

Midge, I. (1953). M.Sc. Thesis, McMaster University, Hamilton, Ontario.

Miesch, A. T. (1976). Q-mode Factor Analysis of Compositional Data: Computers and Geo-sciences, V. 1, p. 147-159.

Milner, C. W. D., M. A. Rogers and C. R. Evans (1977). Petroleum Transformations in Reservoirs: Jour. Geochem. Exploration, V. 7, p. 101-103.

Morrison, R. T. and R. N. Boyd (1968). Organic Geochemistry, Second Edition: Allyn and Bacon, 1204 p.

Muller, E. and J. B. Hyne (1969). Radiochemical (S^{35}) Exchange in the $H_2S + S^{35}$ Reaction: Alberta Sulphur Research Institute,V. VI, No. 1, p. 16-18.

Ohmoto, H. (1972). Systematics of Sulphur and Carbon Isotopes in Hydrothermal Ore Deposits: Econ. Geol., V. 67, No. 5, p. 551-578.

Oil and Gas Conservation Board of Alberta (1970). Pressure - Depth and Temperature - Depth Relationships Alberta Crude Oil Pools: Oil Gas Conservation Board publication #OGCB-70-22, 23 p.

Oppenheimer, C. H. and P. T. Broneer (1963). Introduction to Geological Microbiology: McGraw-Hill, New York.

Orr, W. and A. G. Gaines, JR. (1973). Observations on Rate of Sulphate Reduction and Organic Matter Oxidation in the Bottom Waters of an Estuarine Basin - The Upper Basin of the Pettaquamscutt River (Rhode Island): in Advances in Organic Geochemistry; editors B. Tissot and F. Bienner, Editions Technip, Paris, p. 791-812.

Orr, W. L. (1974). Changes in Sulphur Content and Isotopic Ratios of Sulphur During Petroleum Maturation - Study of Big Horn Basin Paleozoic Oils: Am. Assoc. Pet. Geol., V. 58, No. 11, p. 2295-2318.

Orr, W. L. (1975). Geologic and Geochemical Controls on the Distribution of Hydrogen Sulphide in Natural Gas: Seventh International Meeting on Organic Geochemistry, Madrid; preprint, 20 p.

Oswald, D. H. (1967). International Symposium on the Devonian System: published by the Alta. Soc. Pet. Geol., edited by D. H. Oswald.

Parr Manual No. 130 (1948). Parr Instrument Company, Moline, Illinois, 71 p.

Pepkowitz, L. P. and E. L. Shirley (1951). Micro-Detection of Sulphur: Analytical Chemistry, V. 23, p. 1709.

Postgate, J. (1960). The Economic Activities of Sulphate-Reducing Bacteria: in Progress in Industrial Microbiology, D. J. D. Hochenhull (editor), London, Heywood, V. 2, p. 42-69.

Postgate, J. (1965). Recent Advances in the Study of Sulphate-Reducing Bacteria: Bacteriol Rev., V. 29, p. 425-441.

Prather, R. W. and G. B. McCourt (1968). Geology of Gas Accumulations in Paleozoic Rocks of Alberta Plains: in Natural Gases of North America - A Symposium; Am. Assoc. Pet. Geol., Memoir 9, V. 2, p. 1238-1284.

Price, L. C. (1976). Aqueous Solubility of Petroleum as Applied to its Origin and Primary Migration: Am. Assoc. Pet. Geol., V. 60, p. 213-244.

Pryor, W. A. (1962). Mechanisms of Sulphur Reactions: McGraw-Hill, New York, 241 p.

Racz, D. (1971). The Role of Diffusion Transfer in the Evolution of Heterogeneous Reservoir Systems: Chemical Geology, V. 8, No. 3, p. 171-196.

Rayleigh, J. W. S. (1896). Theoretical Considerations Respecting the Separation of Gases by Diffusion and Similar Processes: Phil. Mag., V. 42, p. 77-107.

Reznikov, A. N. (1967). The Geochemical Conversion of Oils and Condensates in the Zone of Katagenesis: Geol. Nefti Gaza, V. 5, p. 24-28.

Robinson, B. W. and M. Kusakabi (1975). Quantitative Preparation of Sulphur Dioxide, for $^{34}S/^{32}S$ analyses, from Sulphides by Combustion with Cuprous Oxide: Anal. Chem., V. 47, No. 7, p. 1179-1181.

Sackett, W. M. (1968). Carbon Isotope Composition of Natural Methane Occurrences: Am. Assoc. Pet. Geol., V. 52, No. 5, p. 853-857.

Sackett, W. M., S. Nakaparksin and D. Dalrymple (1968). Carbon Isotope Effects in Methane Production by Thermal Cracking: Advances in Organic Geochemistry, Proceedings of the Third International Conference, Edited by G. W. Hodgson, p. 37-53.

Sakai, H. (1968). Isotopic Properties of Sulphur Compounds in Hydrothermal Processes: Geochem. Jour., V. 2, p. 29-49.

Schwarcz, H. P., J. Hoefs and D. Welte (1969). Carbon: Handbook of Geochemistry V. II/1, p. 6-B-1 to I-17., published by Springer-Verlag, Berlin,

Shaw, E. W. (1967). Some General Relationships between Sour Gas Occurrences and the Geological History of the Western Canada Basin: in 3rd Ann. Symposium, Alberta Sulphur Research Institute, p. 5-17.

Silverman, S. R. (1964). Investigation of Petroleum Evolution and Origin by Carbon Isotope Studies: in Isotopic and Cosmic Chemistry; Craig, Miller and Wasserberg (editors) N. Holland, Amsterdam, p. 92-102.

Silverman, S. R. (1965). Migration and Segregation of Oil and Gas: in Fluids in Subsurface Environments, Symposium; A. Young and J. E. Galley (Editors) Am. Assoc. Pet. Geol. Memoir No. 4, p. 53-65.

Silverman, S. R. (1967). Carbon Isotope Evidence for the Role of Lipids in Petroleum Formation: Jour. Am. Chem. Soc., V. 44, p. 691-695.

Silverman, S. R. (1971). Influence of Petroleum Origin and Transformation on Its Distribution in Sedimentary Rocks: Proc. Eighth World Pet. Cong., V. 2, p. 47-54.

Smith, J. E., J. G. Erdman and D. A. Morris (1971). Migration, Accumulation and Retention of Petroleum in the Earth: Proc. Eighth World Pet. Cong., V. 2, p. 13-26.

Speers, G. C. and E. V. Whitehead (1969). Crude Petroleum-Sulphur Compounds: in Organic Geochemistry, Methods and Results, Edited by G. Eglington and M. T. J. Murphy, Springer-Verlag.

Stahl, W. J. (1967). On the Method of C^{12}/C^{13} Isotope Analysis of Natural Gas: Erdoel u. Kohle, Erdgas, Petrochemie, V. 20, No. 8, p. 556-559.

Stahl, W. J. and C. H. Tang (1971). Carbon Isotope Measurements of Methane, Higher Hydrocarbons, and Carbon Dioxide of Natural Gases from Northwestern Taiwan: Pet. Geol. of Taiwan, No. 8, p. 77-81.

Stahl, W. J. (1974). Carbon Isotope Fractionations in Natural Gases: Nature, V. 251, p. 134-135.

Stahl, W. J. (1975). Kohlenstoffisotopenverhaltnisse von Erdgassen: Erdoel u. Kohle, Erdgas, Petrochemie, V. 28, No. 4, p. 188-191.

Stahl, W. J. (1977). Carbon and Nitrogen Isotopes in Hydrocarbon Research and Exploration: Chemical Geology, V. 20, p. 121-149.

Staplin, F. L. (1969). Sedimentary Organic Matter, Organic Metamorphism, and Oil and Gas Occurrence: Bull. Can. Pet. Geol., V. 17, p. 47-66.

Swift, S. C. (1976). Sulphur Bearing Capacity of Hydrogen Sulphide Gas: Jour. Soc. Pet. Eng., V. 16, No. 2, p. 57-64.

Thode, H. G., J. Monster and H. B. Dunford (1958). Sulphur Isotope Abundances in Petroleum and Associated Materials: Am. Assoc. Pet. Geol., V. 42, No. 11, p. 2619-2641.

Thode, H. G. and J. Monster (1965). Sulphur-Isotope Geochemistry of Petroleum, Evaporites and Ancient Seas: Am. Assoc. Pet. Geol., Memoir No. 4 - Fluids in Subsurface Environments, p. 367-377.

Thode, H. G. and J. Monster (1970). Sulphur Isotope Abundances and Genetic Relations of Oil Accumulations in the Middle East Basin: Am. Assoc. Pet. Geol., V. 54, No. 4, p. 627-637.

Thompson et al. (1965). Identification of Some Cyclic Sulphides in a Wasson, Texas Crude Oil Distillate Boiling from 111° to 150°C: Jour. Chem. Eng. Data, V. 10, p. 279.

Toland, W. G. (1960). Oxidation of Organic Compounds with Aqueous Sulphate: Jour. Am. Chem. Soc., V. 82, p. 1911-1916.

Trudinger, P. A., I. B. Lambert and G. W. Skyring (1972). Biogenic Sulphide Ores - A Feasibility Study: Econ. Geol., V. 67, p. 1114-1127

Tudge, A. P. and H. G. Thode (1950). Thermodynamic Properties of Isotopic Compounds of Sulphur: Can. Jour. Res., V. 28B, p. 567-578.

Urey, H. C. (1947). The Thermodynamic Properties of Isotopic Substances: Journal of the Chemical Society, p. 562-581.

Van Everdingen, R. O. (1968). Studies of Formation Waters in Western Canada - Geochemistry and Hydrodynamics: Can. Jour. Earth Sci., V. 5, p. 523-543.

Vredenburgh, L. D. and E. S. Cheney (1971). Sulphur and Carbon Isotope Investigation of Petroleum, Wind River Basin, Wyoming: Am. Assoc. Pet. Geol., V. 55, No. 11, p. 1954-1975.

White, R. J. (1960). Oil Fields of Alberta: R. J. White (editor) published by Alta. Soc. Pet. Geol., 272 p.

Winters, J. C. and J. A. Williams (1969). Microbial Alteration of Crude Oil in the Reservoir: in Symposium on Petroleum Transformation in Geologic Environments - Div. Pet. Chem., Am. Chem. Soc., New York, N.Y., Sept. 7-12, Pap. PETR 86-E22-E31.

Young, A., P. H. Monaghan and R. T. Schweisberger (1977). Calculation of Ages of Hydrocarbon in Oils - Physical Chemistry Applied to Petroleum Geochemistry I: Am. Assoc. Pet. Geol. Bull., V. 61, No. 4, p. 573-600.

APPENDIX I

REAGENTS

1. Reducing Solution

    473 ml HI (S.G = 1.7)

    722 ml concentrated HCl

    232 ml H_3PO_2 (50%)

    Boil for 45 minutes.

2. Cadmium Acetate Solution

    61.5 gm Cadmium acetate

    500 ml Acetic acid (17 N)

    2000 ml distilled water

3. Silver Nitrate Solution (0.5 N)

    170 gm $AgNO_3$

    2000 ml of choride free distilled water

    Store in a colored glass bottle to avoid the photo-decomposition of the solution to native silver.

4. Van Slyke - Folch Oxidizing Solution

    63.90 gm CrO_3

    335 ml 85% H_3PO4

    664 ml fuming sulphuric acid

Heat this mixture to 150°C, stirring frequently until all of the CrO_3 is dissolved. Allow the mixture to cool in a covered container.

APPENDIX II

CALCULATION OF THE EFFECT OF THE PRODUCTION OF CARBON MONOXIDE ON THE C^{13} VALUE OF CARBON DIOXIDE

For the reaction:

$$CO + 2\,CuO \rightleftharpoons CO_2 + Cu_2O \qquad \begin{array}{l} P = 1 \text{ atm.} \\ T = 600°C \end{array} \qquad \text{A-1.}$$

the equilibrium constant is defined as:

$$K_{equ} = \frac{fCO_2 \times aCu_2O}{fCO \times (aCuO)^2} \qquad \text{A-2.}$$

Assuming ideal gas conditions, then:

$$K_{equ} = \frac{PCO_2}{PCO} \cdot \frac{aCu_2O}{(aCuO)^2} \qquad \text{A-3.}$$

Both Cu_2O and CuO are solids and their activities are, by convention, considered to be unity. Therefore,

$$K_{equ} = \frac{PCO_2}{PCO} \qquad \text{A-4.}$$

From classical thermodynamics:

$$n \quad K_{equ} = -\frac{G°}{RT} + \text{constant} \qquad \text{A-5.}$$

For reaction 1, the constant in equation 5 can be evaluated at 25°C. However, H_r^{o} for reaction 1 has to be evaluated at 600°C. H_r^{o} is related to the standard heat capacity of the reaction (C_p^{o}) through the following relationship:

$$\left[\frac{\sigma \Delta H^\circ_r}{\sigma T}\right]_p = \Delta C^\circ_p \qquad P = 1 \text{ atm.} \qquad \text{A-6.}$$

The standard heat capacity for a reaction at any temperature can be calculated from an equation of the form:

$$\Delta C^\circ_p = \Delta a + \Delta b \times 10^{-3}T + \Delta c \times 10^{5}T^{-2} \qquad P = 1 \text{ atm.} \qquad \text{A-7.}$$

where ΔC°_p is defined as the difference between the heat capacities of the reactants and products. The parameters in equation 7 are calculated from equations of a similar form for the reactants and products. That is:

$$C^\circ_p = a + b \times 10^{-3}T + c \times 10^{5}T^{-2} \qquad P = 1 \text{ atm.} \qquad \text{A-8.}$$

Partially integrating equation 6 gives:

$$\Delta H^\circ_r = \Delta C^\circ_p \, dT + \text{constant} \qquad \text{A-9.}$$

Substituting equation 7 into equation 9 and integrating produces:

$$\Delta H^\circ_r = \Delta aT + \frac{\Delta b}{2} \times 10^{-3}T^2 - \frac{\Delta c \times 10^5}{T} + \text{constant} \qquad \text{A-10.}$$

Helgeson (1969) provides heat capacity equations for CO, CuO, CO_2, and Cu_2O. Using these, the standard heat capacity for reaction 1 was determined to be:

$$\Delta C^\circ_p = 9.41 + 2.02 \times 10^{-3}T - 1.95 \times 10^{5}T^{-2} \qquad \text{A-11.}$$

Therefore,

$$\Delta H^\circ_r = 9.41T + 1.01\text{x}10^{-3}T^2 + 1.95\text{x}10^5T^{-1} + \text{constant} \qquad \text{A-12.}$$

At 298°K the constant in equation 12 has a value of -36998.23 calories.

Therefore,

$$\Delta H^\circ_r = 9.41T + 1.01\text{x}10^{-3}T^2 + 1.95\text{x}10^5T^{-1} + 36998.23 \qquad \text{A-13.}$$

Evaluating equation 13 at 873°K, the heat of reaction for reaction 1 has a value of -27790.21 calories. Substituting this number into equation 5 gives:

$$\log K_{equ} = \frac{27790.21}{1.9872 \text{ x } 2.303} \text{ x } \frac{1}{873} + \text{constant} \qquad \text{A-14.}$$

In order to evaluate the constant in equation 14, the equilibrium constant for reaction 1 must be determined at 298°K. Assuming idealality,

$$\ln K_{equ} = \frac{-\Delta G^\circ}{RT} \qquad \text{A-15.}$$

For reaction 1, $\Delta G^\circ = -66070$ calories

Therefore, $\log K_{equ} = \frac{66070}{1.9872 \text{ x } 298 \text{ x } 2.303} = 48.4454$

Therefore, K_{equ} (P = 1 atm., T = 298°K) $3\text{x}10^{48}$

Substituting this value into equation 5, then the constant in equation 14 has a value of 23.91840. Therefore, solving equation 14 at T = 873°K and P = 1 atm. gives a value of 7.484×10^{30} for the equilibrium constant of reaction 1.

Assuming that the vapour pressure of CuO and Cu_2O are minimal at 600°C, then:

$$P_{Total} = PCO_2 + PCO = 1 \text{ atm.} \qquad \text{A-16.}$$

$$K_{equ} = \frac{PCO_2}{PCO} \quad 7 \times 10^{-30} \qquad \text{A-17.}$$

The simultaneous solution of equations 16 and 17 gives a value of 7×10^{-30} atm. for the partial pressure of carbon monoxide at reaction temperatures and pressures.

The internal volume of the reaction system is approxiamately 12.3 cc. Using the ideal gas law (PV = nRT), the number of moles of carbon monoxide and carbon dioxide were calculated from their partial pressures to be 1.20×10^{-32} and 1.72×10^{-4}, respectively. Converting these to mole fractions, then $X_{CO2} = 1$ and $X_{CO} = 6.98 \times 10^{-38}$. Here, X designates mole fraction. Using a relationship similar to the one defined for sulphur by Ohmoto (1972), then:

$$\delta C^{13}_{\text{Total Carbon}} = X_{CO_2} \cdot \delta C^{13}_{CO_2} + X_{CO} \cdot \delta C^{13}_{CO} \qquad \text{A-18.}$$

At 600°C the equilibrium carbon isotope fractionation factor between CO and CO_2 is 1.018 (Urey, 1946; Bottinga, 1968; and Schwartz, 1969). Accepting that the average C^{13} value of CO_2 derived by oxidizing Devonian oil is -21·8‰ (Degens, 1969), then CO in equilibrium with the CO_2 will have a δC^{13} value of -46‰. Substituting the del values and mole fractions into equation 18 gives:

$$\delta C^{13}_{\text{Total Carbon}} = -28(1) + -46(6.98\text{x}10^{-38})$$
$$= -28‰$$

Therefore, the mole fraction of carbon monoxide produced during the Carius tube oxidation reaction is not great enough to negate the relationship that, within experimental error:

$$\delta C^{13}_{\text{Total oxidized carbon}} = \delta C^{13}_{CO_2}$$

and therefore,

$$\delta C^{13}_{CO2} = \delta C^{13}_{\text{oil}}$$

APPENDIX III

CALCULATION OF THE ISOTOPE EFFECT OF CONTAMINANT ATMOSPHERIC CARBON DIOXIDE ON THE DEL VALUE OF CARBON DIOXIDE PRODUCED BY THE CARIUS TUBE OXIDATION OF OILS

Atmospheric carbon dioxide was frozen down onto the oil impregnated cupric oxide during the freezing period prior to the second evacuation of the carius tube (refer to Chapter I, Section 4). This carbon dioxide was extracted from about a 25 cc volume which included the reaction vessel and part of the extraction apparatus. If all of the carbon dioxide in this volume was frozen out, and if it can be assumed that at one atmosphere pressure and 25°C the air contains 0.03 volume percent carbon dioxide, then the number of moles of contaminant carbon dioxide can be calculated as:

$$\text{moles contaminant } CO_2 = \frac{0.025 \times 0.0003}{22.4} \times \frac{273}{298} = 3.067 \times 10^{-7}$$

The smallest oil sample oxidised gave 1 standard cc of carbon dioxide after complete combustion, or 4.464×10^{-5} mole CO_2. After combustion, the total number of moles of carbon dioxide in the reaction vessel is therefore, 4.497×10^{-5}. Converting to mole fractions, then:

$$X_{CO_2} \text{ of combustion} = 0.993 \text{ and } X_{\text{atmospheric } CO_2} = 0.007$$

where X designates mole fraction. With reference to Ohmoto (1972):

$$\delta C^{13}_{CO_2\text{-mix}} = X_{CO_2\text{-comb.}} \, \delta C^{13}_{CO_2\text{-comb.}} + X_{CO_2\text{-atm.}} \, \delta C^{13}_{CO_2\text{-atm.}} \qquad \text{A-22.}$$

Assuming that $\delta C13_{atm\text{-}CO_2}$ has the value of East Pacific air, which is -7.1‰ PDB and assuming that the del value of the carbon dioxide produced from the combustion of the oil is -28‰, then these values together with the mole fractions can be substituted into equation A-22. The solution of equation A-22. gives a value of -27.9‰. Considering that the analytical error is ±0.2‰, then the δC^{13} value of the mixture can be accepted as the δC^{13} value of the carbon dioxide derived from the carius tube oxidation of the oil.

APPENDIX IV

SAMPLE GAS TRANSFER PROCEDURE

Refer to Figure A-1

1. Place a steel weight gently over the breakseal of the glass storage bottle and fuse the storage bottle onto the gas transfer line using an oxygen-methane torch.

2. Turn both of the two-way greased stopcocks of the injection U-tube to the A to B flow position. Connect the U-tube onto the transfer apparatus at the ultra torr union outlet.

3. Open stopcock 1 and pump the line down to high vacuum by opening stopcock 2.

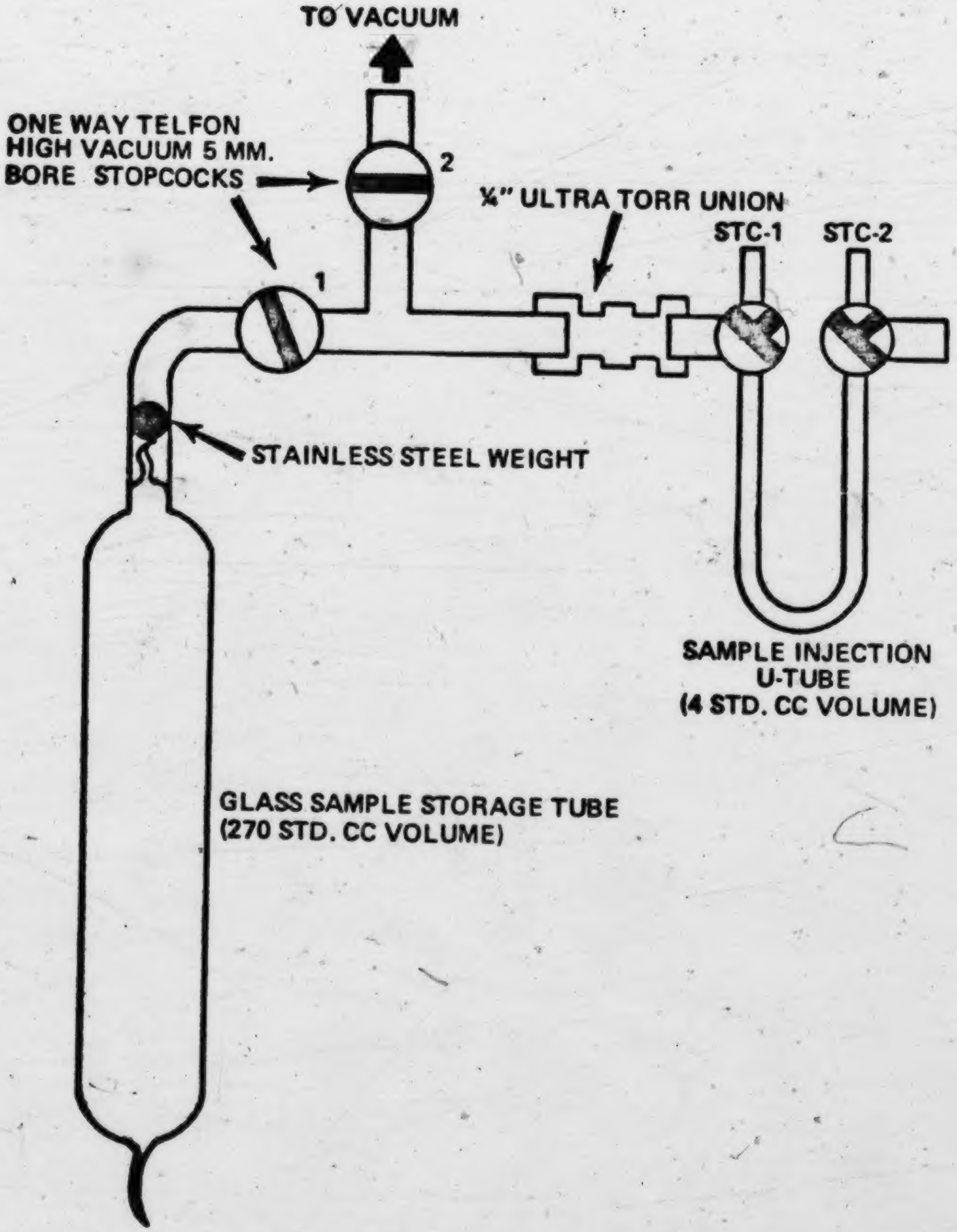
4. Once high vacuum is reached, close stopcock 1 and shatter the glass breakseal using the steel weight. The sample gas will expand up to stopcock 1.

5. Close stopcock 2.

6. Gently secure the sample U-tube against the ultra torr union. This prevents the U-tube from being blown out by excessive gas pressure when stopcock 1 is opened.

FIGURE A-1

SAMPLE TRANSFER APPARATUS


TO VACUUM
ONE WAY TELFON
HIGH VACUUM 5 MM.
BORE STOPCOCKS
2
1
¼" ULTRA TORR UNION
STC-1
STC-2
STAINLESS STEEL WEIGHT
SAMPLE INJECTION
U-TUBE
(4 STD. CC VOLUME)
GLASS SAMPLE STORAGE TUBE
(270 STD. CC VOLUME)

7. Open stopcock 1. Gas now will expand into the injection U-tube. After equilibrium is reached, close stopcock 1.

   The sample U-tube and vacuum line now contains an aliquot of gas at a pressure in excess of one atmosphere. As a result, the U-tube contains a gas sample whose volume is greater that 4 std. cc.

8. Rotate injection U-tube stopcock, STC-1, to the B to C flow position. During the rotation the U-tube was momentarily exposed to atmosphere, through the A to C path, and its pressure therefore reduced to ambient values (app. 1 atm.). The U-tube and its contained 4 std. cc. gas sample can now be taken to the chromatograph for injection.

This expansion transfer procedure was developed to replace the more commonly used mercury Toepler pump technique because of the high hydrogen sulphide contents of many of the natural gases to be analysed for this thesis.

APPENDIX V

SAMPLE GAS INJECTION PROCEDURE

Refer to Figure A-2 and Table A-I

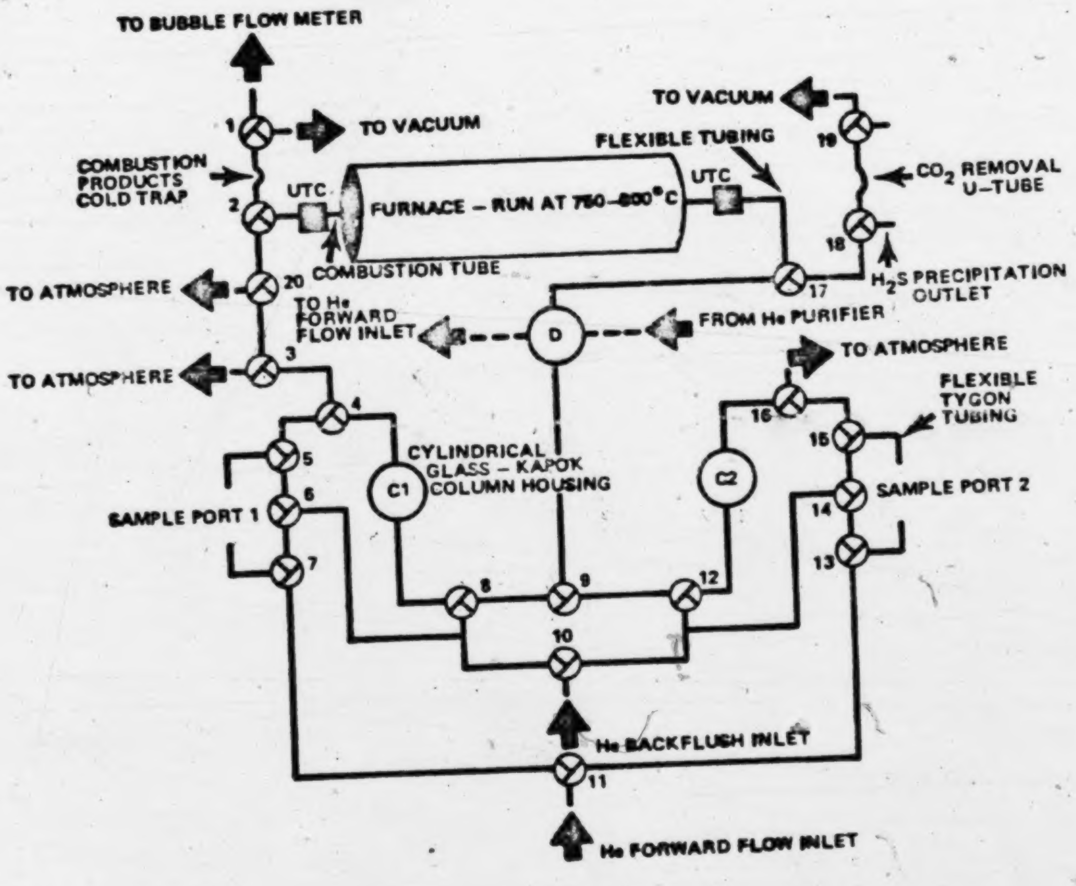
1. Using tygon tubing of an appropriate inner diameter, attach the injection U-tube to chromatograph port 1 or port 2, whichever is part of a backflushing system.

   Consider column 2 (C2 in Figure A-2) to be backflushing. Table A-I lists the appropriate flow positions for the two-way stopcocks of the chromatograph system. Before the gas sample can be introduced to the flow system, air must be purged from the by-pass flow line between stopcocks 15 and 13 and the sample U-tube stopcocks. To do this:

   A. Divert the helium backflush flow from column C2 by turning stopcock 12 to the (closed) A to C flow position.

   B. Turn stopcocks 14 and 15 to the B to C flow position. Air between stopcock 15 and the U-tube is now flushed to atmosphere by a rapid helium flow. After 20 seconds stop the helium flow by placing your finger over the end of the U-tube stopcock outlet to atmosphere. With flow stopped, quickly turn this U-tube stopcock to the A to B flow position. In every case, FIGURE A-2

NATURAL GAS COMPONENT SEPARATION AND COMBUSTION APPARATUS


TO BUBBLE FLOW METER
1
TO VACUUM
COMBUSTION PRODUCTS COLD TRAP
2
UTC
FURNACE – RUN AT 750–800°C
COMBUSTION TUBE
FLEXIBLE TUBING
UTC
TO VACUUM
19
CO2 REMOVAL U–TUBE
18
H2S PRECIPITATION OUTLET
17
TO ATMOSPHERE
20
TO He FORWARD FLOW INLET
D
FROM He PURIFIER
TO ATMOSPHERE
3
4
TO ATMOSPHERE
16
FLEXIBLE TYGON TUBING
15
5
6
SAMPLE PORT 1
7
C1
CYLINDRICAL GLASS – KAPOK COLUMN HOUSING
C2
SAMPLE PORT 2
14
13
8
9
12
10
He BACKFLUSH INLET
11
He FORWARD FLOW INLET

LEGEND

UTC: ULTRA TORR CONNECTOR (¼")

D : THERMAL CONDUCTIVITY DETECTOR

C : 6' POROPAC Q COLUMN –
STANDARD WALL 8 MM OD PYREX

⊗ : 2 MM 2-WAY GROUND GLASS STOPCOCK

FLOW LINE MADE OF 8 MM OD PYREX

TABLE A-I

List of Stopcock Settings for the Chromatograph and Combustion Apparatus

(Refer to Figure A-2)

Column 1 - forward flow through the furnace tube, and Column 2 - backflush

Stopcock Number	Stopcock Flow Path
1	A to C
2	B to A
3	Closed to Flow
4	A to C
5	B to C
6	Closed to Flow
7	A to B
8	A to C
9	A to B
10	B to A
11	B to C
12	B to A
13	Closed to Flow
14	Closed to Flow
15	Closed to Flow
16	A to B
17	A to B
18	C to B
19	Closed to Flow
20	Closed to Flow

Column 1 - backflush, and Column 2 - forward flow through the furnace tube

Stopcock Number	Stopcock Flow Path
1	A to C
2	B to A
3	A to C
4	C to B
5	Closed to Flow
6	Closed to Flow
7	Closed to Flow
8	B to C
9	C to B
10	B to C
11	B to A
12	A to C
13	C to B
14	Closed to Flow
15	B to A
16	A to C
17	A to B
18	C to B
19	Closed to Flow
20	Closed to Flow

the built up pressure at the finger exceeded one atmosphere and therefore none of the gas sample was lost during the rotation of the U-tube stopcock.

C. Rotate stopcock 15 to the A to C position.

D. Rotate stopcocks 14 and 13 to the A to B flow position. Air is now flushed from the line between stopcock 13 and the other U-tube stopcock. Again, after 20 seconds stop the helium flow using your finger and quickly rotate the U-tube stopcock to the B to C position.

E. Turn stopcock 13 and 14 to the A to C flow position. The sample is now ready to be injected into chromatograph column C2.

2. Change column C2 to a forward flow status and column C1 to a backflush status (see Table A-I).

3. Bring column C2 to a temperature of 35°C using an appropriate hot and cold water mixture.

4. Adjust the helium flow to 60 ml/min.

5. Check the furnace temperature to make certain that it is in a range from 750°C to 800°C. The furnace generally took 2 hours to reach a

steady state temperature of 800°C. This heating was done from 6:00 a.m. to 8:00 a.m. when the line was not in use. A timer was used to turn the furnace on in the morning.

6. Flush the sample from the injection U-tube into C2 by simultaneously turning stopcocks 13 and 15 to the C to B and B to A flow positions, respectively.

The sample injection is recorded on the chromatograph chart as a recorder pen deflection caused by a gas pressure surge created by stopping, then starting the helium flow as two-way stopcocks 13 and 15 were rotated.

APPENDIX VI

THE PROCEDURE FOR THE ISOLATION AND PURIFICATION OF COMBUSTION PRODUCTS

Refer to Figure A-3

Prior to running a gas sample in the chromatograph, open stopcocks V2, V3, V4, V7, V8, V9, V11, and V12. Stopcocks V1 and V10 should be closed. Pump the entire line to high vacuum. Repair any leaks at this time, as there is very little time for repairs during runs.

Once the water and carbon dioxide from the oxidation of a gas component are frozen over into the combustion products U-tube, the purification procedure can begin.

1. Divert the helium flow from the furnace through stopcock 20 to atmosphere by turning stopcock 2 to the B to A flow position (see Figure A-3).

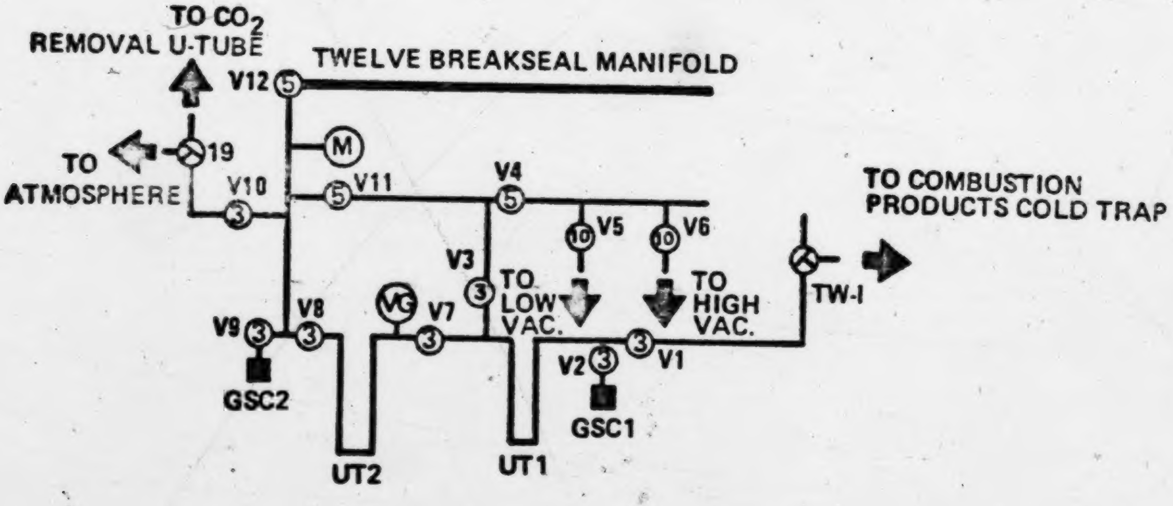
2. Close vacuum stopcocks V2, V7, V9, and V11. Open V5 and close V6.

3. Top up the nitrogen in the dewar around the combustion products cold trap. Open stopcock V1.

4. Open two-way stopcock 1 to the C to B position. Helium is now pumped out of the combustion products U-tube by low vacuum. Once a

FIGURE A-3

COMBUSTION PRODUCTS SEPARATION LINE


TO CO_2 REMOVAL U-TUBE
TWELVE BREAKSEAL MANIFOLD
V12
M
TO ATMOSPHERE
19
V10
V11
V4
V5
V6
TO COMBUSTION PRODUCTS COLD TRAP
V3
TO LOW VAC.
TO HIGH VAC.
TW-I
V9
V8
VG
V7
V2
V1
GSC2
GSC1
UT2
UT1

LEGEND

⑤ : 5 MM TEFLON HIGH VAC-STOPCOCK
GSC : GAS STORAGE CONTAINER
UT : U-TUBE COLD TRAP
M : MERCURY MANOMETER
VG : VACUUM GAUGE

good low vacuum is reached, close V5 and open V6. Pump the combustion products U-tube to near high vacuum.

5. Apply a dewar of liquid nitrogen to U-tube 1. Close V3.

6. Remove the dewar of liquid nitrogen from the combustion products cold trap and gently warm this to room temperature. To aid the transfer of combustion products to U-tube 1, gently flame the glass line along the transfer path.

7. Once transfer is complete, close V1. The vacuum line is now isolated from the chromatograph line.

8. Turn two-way stopcock 1 to the A to C flow position and stopcock 2 to the B to A flow position. This diverts the helium flow from the furnace tube back through the combustion products U-tube to atmosphere. Close stopcock 20 (see Figure A-3). Combustion products from another hydrocarbon component are now ready to be trapped.

9. Slowly open V3 and gradually pump on the frozen down water and carbon dioxide, in U-tube 1, to high vacuum. This removes any impurities that were frozen down as a clathrate with the combustion products in the first cold trap.

10. Close V3 and open V11.

11. Remove the liquid nitrogen dewar from U-tube 1 and warm the U-tube to room temperature. Apply this dewar of liquid nitrogen to U-tube 2. Place a dewar containing an acetone-dry ice slush on U-tube 1.

12. After all of the water is frozen out into U-tube 1, close V8 and open V7. Monitor the CO_2 transfer to U-tube 2 with the vacuum gauge.

13. When the vacuum reading is steady at near high vacuum, briefly open V8 and close it. Close V7.

14. Remove the acetone-dry ice and liquid nitrogen dewars from U-tube 1 and U-tube 2. Warm these U-tubes to room temperature.

15. Place a cold cup of liquid nitrogen on the manometer cold finger. Close V12 and V11. Open V8 and transfer the CO_2 in U-tube 2 to mercury manometer. Monitor this transfer with the vacuum gauge.

16. When the transfer is complete, close the manometer stopcock and open V12 and V11. Remove the manometer cold cup and warm the cold finger to room temperature. Record the mercury level. If the volume of CO_2 is less than 1 std. cc., transfer both the water and CO_2 to gas storage container GSC2. If the CO_2 is equal to or in excess of 1 std. cc., the gas can be freeze transferred from the manometer through V12 to a breakseal.

17. Once the CO_2 has been frozen over to a breakseal, and this drawn off, the water in U-tube 1 can be transferred directly to a breakseal for storage.

Any gas stored in GSC 2 or GSC1 can be added to from a second run after the first sample has been fully processed.

Vacuum stopcocks V10 and V19 remain closed throughout the isolation and purification procedures. These stopcocks connect the chromatograph line to the vacuum line and serve to transfer the CO_2 component of the natural gas to the vacuum line for purification and storage for isotopic analysis. The carbon dioxide component was generally too low in abundance in the natural gas samples to warrant consideration in this study.

Appendix VII

Oil Component Analyses Expressed as a Percentage of the Topped Oil

Pool - Field		Well Location	Saturate	Aromatic	Maltene	NSO	Total	Not Analysed
Big Lake	D-3	13-23-53-26W4	46.5	33.8	2.2	9.6	92.1	7.9
			45.9	32.6	2.7	9.6	90.8	9.2
		9-26-53-26W4	47.3	33.4	3.6	9.7	94.0	6.0
Acheson	D-3	4-10-52-26W4	59.3	27.4	2.3	5.7	94.7	5.3
Yekau Lake	D-3	8-4-52-26W4	57.9	25.8	2.4	6.2	92.3	7.7
Leduc Woodbend	D-3	13-3-50-26W4	58.4	27.0	2.6	6.0	94.0	6.0
		8-9-50-26W4	57.0	24.9	4.0	6.7	92.6	7.4
			55.3	22.8	2.7	6.8	87.6	12.4
		8-5-51-26W4	56.8	24.1	2.6	6.2	89.7	10.3
Golden Spike	D-3	12-26-51-27W4	50.5	28.8	4.1	8.0	91.4	8.6
			48.6	28.4	3.0	8.4	88.4	11.6
		10-27-51-27W4	50.8	29.1	3.7	7.7	91.3	8.7
Wizard Lake	D-3	1-21-48-27W4	54.0	27.7	3.3	8.0	93.0	7.0
			53.7	26.6	4.2	7.5	92.0	8.0
			51.4	25.0	3.1	7.4	86.9	13.1

Pool - Field		Well Location	Saturate	Aromatic	Maltene	NSO	Total	Not Analysed
Glen Park	D-3	4-2-49-27W4	55.1	28.6	3.1	6.3	93.1	6.9
		5-2-49-27W4	54.4	27.5	3.8	6.9	92.6	7.4
			52.8	25.9	3.0	7.3	89.0	11.0
Bonnie Glen		14-6-47-27W4	62.5	26.0	1.8	3.0	93.3	6.7
			62.3	24.5	1.9	4.7	93.4	6.6
Sylvan Lake	D-3	10-20-37-3W4	55.0	24.1	2.1	5.7	86.9	13.1
		10-17-37-3W4						
Westerose	D-3	4-3-46-28W4	61.1	21.9	1.4	4.0	88.4	11.6
			64.3	24.4	1.8	3.9	94.4	5.6
West Drumheller	D-3	11-1-30-21W4	45.0	31.8	2.9	9.4	89.1	10.9
		12-1-30-21W4	45.8	32.7	2.9	9.4	90.8	9.2
New Norway	D-3	11-36-44-22W4	40.2	35.3	3.7	11.4	90.6	9.4
Buffalo Lake	D-3	4-35-39-21W4	28.3	43.1	4.3	11.7	87.4	12.6
Bashaw	D-3	10-6-42-22W4	53.1	26.7	2.1	6.1	88.0	12.0
Erskine	D-3	2-7-39-20W4	32.3	45.1	5.9	8.9	92.2	7.8
			31.0	43.3	5.6	10.2	90.1	9.9
		6-19-39-20W4	31.3	42.5	5.6	10.8	90.2	9.8
			29.6	43.6	5.1	11.8	90.1	9.9

Pool - Field		Well Location	Saturate	Aromatic	Maltene	NSO	Total	Not Analysed
Erskine	D-3	8-13-39-21W4	30.8	42.9	4.2	11.4	89.3	10.7
		8-26-39-21W4	29.9	42.9	4.9	13.1	90.8	9.2
			29.8	42.9	5.3	12.8	90.8	9.2
Stettler	D-3	12-3-38-20W4	29.9	40.8	7.3	12.7	90.7	9.3
			28.8	41.2	6.5	12.9	89.4	10.6
		16-9-38-20W4	29.9	41.6	4.4	11.8	87.7	12.3
		16-16-38-20W4	30.5	41.6	6.7	11.8	90.6	9.4
Malmo	D-3	5-14-44-22W4	48.4	30.3	3.0	8.7	90.4	9.6
Clive	D-3A	16-29-40-24W4	59.9	22.6	1.7	4.9	89.1	10.9
		12-33-40-24W4	55.3	23.4	1.8	4.7	85.2	14.8
Wimborne	D-3	6-11-33-26W4	55.8	29.1	1.6	4.3	90.8	9.2
			55.5	25.8	0.9	5.3	87.5	12.5
		10-13-33-26W4	54.8	28.9	1.1	4.6	89.4	10.6

- Keg River Oil Analyses -

Zama Keg River		6-23-116-4W6	42.7	39.0	2.9	9.2	93.8	6.2
		12-21-117-4W6	45.0	38.0	3.7	7.3	94.0	6.0
		2-25-117-5W6	46.7	37.0	3.8	7.1	94.6	5.4

Pool - Field	Well Location	Saturate	Aromatic	Maltene	NSO	Total	Not Analysed
Keg River Oil Analyses - Cont'd							
Virgo Keg River	5-27-114-5W6	48.4	32.0	1.8	5.9	88.1	11.9
	5-11-115-5W6	48.0*	32.1	2.1	4.7	86.9	13.1

*Adjusted value.

Appendix VIII

Carbon Isotopes⁺ of Devonian Associated Oils and Gases

Pool Name		Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Big Lake	D-3	13-26-53-26W4	58	-27.5	-29.1	-25.9	-45.2	-35.5	-32.1
				-27.5					
		13-25-53-26W4		-27.1	-28.7	-26.5	-45.5	-35.8	-31.6
				-27.1	-29.1	-26.3			
Acheson	D-3	4-10-52-26W4	60	-28.5	-29.4	-28.2	-43.8	-35.2	-32.1
Yekau Lake	D-3	8-4-52-26W4	63	-28.5	-29.5	-28.3	-43.6	-34.8	-32.0
Leduc Woodbend	D-3	13-3-50-26W4	66	-28.2	Lost	-27.9	-43.4	-34.1	-30.3
				-28.3					
				-28.3					
		8-5-51-26W4		-28.6	-29.5	-28.2	-43.8	-34.5	-30.4
				-28.2	-	-28.5		-34.5	-30.6
		8-9-50-26W4		-28.5	-29.2	-28.3	-43.5	-34.2	-30.7
				-28.4	-29.3	-28.2			

⁺All δC^{13} values are given in reference to the Chicago PDB standard.

δC^{13} is defined as $\delta C^{13} = \frac{C^{13}/C^{12}\text{ sample}}{C^{13}/C^{12}\text{ std}} - 1 \quad 1000$. It has units of per mil ($^{o}/oo$).

Pool Name		Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Golden Spike	D-3	12-26-51-27W4	67	-27.4	-28.5	-26.2	-	-	-
					-28.9	-26.4	-	-	-
		10-27-51-27W4		-27.2	-28.7	-26.5	-45.9	-35.7	-32.1
Wizard Lake	D-3	1-21-48-27W4	72	-28.3	-29.3	-27.5	-45.1	-35.9	-29.9(?)
				-28.3	-	-27.5			
Glen Park	D-3	4-2-49-27W4	74	-28.1	-28.9	-27.2	-45.1	-35.6	-31.1
		5-2-49-27W4		-27.9	-29.1	-26.8	-44.8	-35.5	-31.4
					-28.7	-27.2			
					-29.1	-26.9			
Bonnie Glen	D-3	14-6-47-27W4	77	-	-29.5	-28.1	-44.7	-33.9	-
					-29.5	-28.4			
						-27.9			
Sylvan Lake	D-3	Separator Sample	79	-	-	-	-41.2	-32.3	-
				-	-	-	-41.4	-32.0	-29.3
Westerose	D-3	Battery Sample	82	-28.4	-29.3	-28.0	-	-	-
		4-3-46-28W4			-29.4	-28.1	-	-	-
		GOC West. Carl 12		-	-	-	-45.1	-33.4	-29.1
		GOC West. Fiveland 6		-	-	-	-44.7	-35.5	-32.1
West Drumheller	D-3	11-1-30-21W4	57	-	-29.9	-27.8	-51.4	-38.3	-35.6
		12-1-30-21W4		-	-30.3	-27.7	-52.1	-39.0	-36.2
									-36.0

Pool Name		Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
New Norway	D-3	11-36-44-22W4	58	-	-28.4	-27.3	-45.9	-38.7	-33.8
Buffalo Lake	D-3	4-35-39-21W4	57	-	-29.7	-24.8	-43.7	-36.8	-33.0
						-25.5			
Bashaw	D-3	10-6-42-22W4	61	-	-29.6	-26.7	-43.0	-36.1	-31.0
Erskine	D-3	2-7-39-20W4	62	-26.6	-28.5	-26.4	-42.5	-35.6	-32.0
						-26.2			
						-26.2			
		6-19-39-20W4		-27.3	-28.8	-26.8	-42.6	-35.6	-32.1
				-27.9		-26.7			
		8-13-39-21W4		-	-28.8	-26.4	-42.8	-36.2	-32.5
		8-26-39-21W4		-	-29.1				
					-29.2	-27.0	-42.5	-35.8	-32.2
						-26.9			
Stettler	D-3	12-3-38-20W4	63	-27.1	-29.0	-27.5	-	-	-
				-27.5		-27.0			
		16-9-38-20W4		-27.8	-29.1	-26.7	-46.3	-38.9	-35.0
				-27.5					
		16-16-38-20W4		-	-28.7	-26.4	-46.1	-38.7	-34.9
				-	-28.5	-	-	-	-
Malmo	D-3	5-14-44-22W4	63	-	-30.0	-	-45.0	-37.7	-33.8
		2-23-44-22W4					-44.9	-37.9	-33.8

Pool Name		Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Clive	D-3	16-29-40-24W4	66	-	-29.6	-27.9	-41.7	-34.8	-30.4
		12-33-40-24W4		-	-29.4	-27.7	-42.2	-35.4	-31.0
Wimborne	D-3	4-1-33-26W4	79	-	-	-	-40.4	-32.7	-
		6-11-33-26W4		-	-29.1	-28.2	-	-	-
				-	-29.0				
		10-13-33-26W4		-	-29.1	-28.0	-	-	-
		7-26-33-26W4		-	-	-	-39.9	-	-
							-40.1	-	-
Zama Keg River		6-23-116-4W6		-	-29.2	-27.3	-	-	-
		7-7-116-5W6		-28.1	-	-	-50.9	-40.2	-33.4
		4-36-116-6W6		-27.9	-28.7	-27.6	-49.8	-38.2	-32.4
		12-21-117-4W6		-27.9	-28.9	-27.8	-44.8	-40.5	-34.0
				-28.0					
		2-25-117-5W6		-	-29.2	-27.7	-55.7	-39.9	-32.7
Virgo Keg River		4-6-115-5W6		-28.8	-30.0	-28.3	-51.6	-39.7	-32.9
				-28.6	-29.7				
		5-11-115-5W6		-28.4	-29.5	-27.9	-	-	-
				-28.4					
		5-27-115-5W6		-28.2	-29.3	-27.7	-39.5	-38.0	-34.3(?)
Rainbow Keg River		8-32-111-7W6		-28.6	-29.7	-28.0	-	-	-
				-28.8					

Appendix VIII

Carbon Isotopes of Devonian Non-Associated Gases

Pool Name		Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Ricinus	D-3	7-13-36-10W5	107				-40.5	--	--
							-40.5		
		10-33-36-10W5					-40.1	--	--
							-40.1		
Strachan	D-3	10-31	124				-36.8	--	--
							-36.8		
		7-32					-38.1	-27.2	-24.1
Harmattan E.	D-3	10-11-32-3W5	110				-31.1		
							-31.2		
Pine Creek	D-3	10-16	117				-36.6	--	--
							-36.5		
		10-23					-37.0	--	--
							-37.0		
Pine N.W.	D-3		119				-33.9		
							-33.8		

Pool Name	Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Beaver River Nahanni	Amoco B.R. A2	171				-30.8	--	--
						-31.0	--	--
	A3					-30.8	--	--
						-30.9	--	--
	A5					-31.0	--	--
						-31.0	--	--
	B1					-31.0	--	--
						-31.0	--	--
	B2					-30.8	--	--
						-30.8	--	--

Appendix VIII

Carbon Isotopes of Miscellaneous Gases

Pool Name	Well Description	Reservoir Temp °C	δC^{13} Oil	δC^{13} Saturates	δC^{13} Aromatics	δC^{13} CH_4	δC^{13} C_2H_6	δC^{13} C_3H_8
Aitken Halfway ss.	D-34 L					-47.2	-31.7	-28.2
Giroux Viking	4-9-66-21W5					-53.1	-30.4	-28.5
Harmattan E. Elkton	10-11-32-3W5	88				-45.2	-30.4	-28.2
Lookout Butte Rundle	PC-73-58	88				-47.7	-32.9	-27.5
Pincher Creek Rundle	PC-73-61	88				-42.8	-31.0	--
Wildmint Halfway	b-66 A					-39.6	--	--

APPENDIX IX

CALCULATION OF THE ACTIVATION ENERGY AND PRE-EXPONENTIAL FACTOR FOR THE REDUCTION OF SULPHATE BY HYDROCARBON

The following calculations used experimental data from Dhannoun and Fyfe (1972). They studied the reaction of gypsum with trimethyl pentane at temperatures in the range of 340°C to 380°C. Table A-2 lists the fraction of sulphate remaining after specified lengths of time at the temperatures of 370°C and 380°C.

Assuming that this reaction is first order, then the following rate equations apply:

$$-\frac{dc}{dt} = Kc \qquad \text{A-19}$$

$$f = e^{-kt} \quad \text{(integrated form of equation A-19)} \qquad \text{A-20}$$

$$k = -\frac{\ln f}{t} \quad \text{(logarithmic transform of equation A-20)} \qquad \text{A-21}$$

Where K and C are, respectively, the rate constant and the concentration. f is the fraction of reactant remaining and t is the time in seconds.

The rate constants in column 3 of Table A-II were determined using equation A-21. The constant values of K after a reasonable extent of reaction supports the assumpation that the reaction rate is first order (Barrow, 1964). Average rate constants were calculated from K's at times past 600 secs. at 380°C and past 1800 secs. at 370°C. $K_{av.}370$ and $K_{av.}380$ were determined to be 6.265×10^{-9} and 1.193×10^{-8}, respectively. Substituting these two values with their appropriate temperatures, into the linear logarithmic transform of the Arrhenius equation $\ln A - \frac{Ea}{RT} = \ln K$), two simultaneous equations in two unknowns were defined. The solution of these two equations gave the following values for the activation energy (Ea) and the pre-exponential factor (A) for the reduction of sulphate by trimethyl pentane:

$Ea = 54{,}000$ calories

$A = 1.171 \times 10^{10}$

where A is the pre-exponential factor

Ea is the activation energy

K is the rate constant

R is the gas constant, whose value is 1.9872 ca./deg.-mole

T is the temperature in °Kelvin

Such values for E_a and A would not result in the production of significant quantities of hydrogen sulphide at temperatures common to the Leduc reservoirs, that is temperatures of less than 150°C, over geologically meaningful periods of time. For example, the extent of sulphate reduced to hydrogen sulphide over a period of time from the Cretaceous to the

TABLE A-II

DATA FROM DHANNOUN AND FYFE (1972)

Temperature = 380°C

Time (secs.)	Fraction of Reactant Left	K
600	0.9999979	3.500×10^{-9}
1080	0.9999896	9.6296×10^{-9}
1380	0.9999826	1.2464×10^{-8}
1800	0.9999817	1.0167×10^{-8}
2220	0.9999687	1.4099×10^{-8}
2700	0.9999729	1.0037×10^{-8}
3000	0.9999669	1.1034×10^{-8}
3900	0.9999435	1.2755×10^{-8}
4320	0.9999449	1.2755×10^{-8}
4800	0.9999390	1.2813×10^{-8}
5100	0.9999396	1.1843×10^{-8}

$K_{av.380} = 1.1933 \times 10^{-8}$

Temperature = 370°C

600	0.9999988	2.0000×10^{-9}
1200	0.9999981	1.5833×10^{-9}
1800	0.9999961	2.1667×10^{-9}
2400	0.9999868	5.5000×10^{-9}
3000	0.9999851	4.9667×10^{-9}
3900	0.9999796	5.2308×10^{-9}
4320	0.9999744	5.9260×10^{-9}
4800	0.9999648	7.3334×10^{-9}
5760	0.9999657	5.9549×10^{-9}
7200	0.9999356	8.9447×10^{-9}

$K_{av.370} = 6.2652 \times 10^{-9}$

present (130 m years) at a temperature of 150°C can be calculated using equations A-20 and A-21. Only 1% of the sulphate had been reduced. At a more common reservoir temperature of 100°C and over the same period of time, virtually none of the sulphate would be reduced.